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Imię i nazwisko autora rozprawy: mgr inż. Karolina Delińska
Dyscyplina naukowa: Chemia

ROZPRAWA DOKTORSKA

Tytuł rozprawy w języku polskim: Metoda opracowania uniwersalnej osnowy na bazie krzemionki do unieruchomienia cieczy jonowych jako materiałów sorpcyjnych w technice mikroekstrakcji do fazy stacjonarnej.

Tytuł rozprawy w języku angielskim: The development of a universal silica-based matrix for the confinement of ionic liquids as sorption materials in the solid-phase microextraction technique.

Promotor *podpis*
Dr hab. inż. Adam Kloskowski

Gdańsk, rok 2022

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OŚWIADCZENIE

Autor rozprawy doktorskiej: mgr inż. Karolina Delińska

Ja, niżej podpisany(a), wyrażam zgodę na bezpłatne korzystanie z mojej rozprawy doktorskiej zatytułowanej:

Metoda opracowania uniwersalnej osnowy na bazie krzemionki do unieruchomienia cieczy jonowych jako materiałów sorpcyjnych w technice mikroekstrakcji do fazy stacjonarnej.

do celów naukowych lub dydaktycznych.[1]

Gdańsk, dnia ....
podpis doktoranta

Świadomy(a) odpowiedzialności karnej z tytułu naruszenia przepisów ustawy z dnia 4 lutego 1994 r. o prawie autorskim i prawach pokrewnych (Dz. U. z 2006 r., nr 90, poz. 631) i konsekwencji dyscyplinarnych określonych w ustawie Prawo o szkolnictwie wyższym (Dz. U. z 2012 r., poz. 572 z późn. zm.),[2] a także odpowiedzialności cywilno-prawnej oświadczam, że przedkładana rozprawa doktorska została napisana przeze mnie samodzielnie.

Oświadczam, że treść rozprawy opracowana została na podstawie wyników badań prowadzonych pod kierunkiem i w ścisłej współpracy z promotorem dr hab. inż. Adamem Kloskowskim.

Niniejsza rozprawa doktorska nie była wcześniej podstawą żadnej innej urzędowej procedury związanej z nadaniem stopnia doktora.

Wszystkie informacje umieszczone w ww. rozprawie uzyskane ze źródeł pisanych i elektronicznych, zostały udokumentowane w wykazie literatury

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[1] Zarządzenie Rektora Politechniki Gdańskiej nr 34/2009 z 9 listopada 2009 r., załącznik nr 8 do instrukcji archiwalnej PG.

[2] Ustawa z dnia 27 lipca 2005 r. Prawo o szkolnictwie wyższym: Rozdział 7 Odpowiedzialność dyscyplinarna doktorantów, Art. 226.

odpowiednimi odnośnikami zgodnie z art. 34 ustawy o prawie autorskim i prawach pokrewnych.

Potwierdzam zgodność niniejszej wersji pracy doktorskiej z załączoną wersją elektroniczną.

Gdańsk, dnia ....

podpis doktoranta

Ja, niżej podpisany(a), wyrażam zgodę na umieszczenie ww. rozprawy doktorskiej w wersji elektronicznej w otwartym, cyfrowym repozytorium instytucjonalnym Politechniki Gdańskiej, Pomorskiej Bibliotece Cyfrowej oraz poddawania jej procesom weryfikacji i ochrony przed przywłaszczaniem jej autorstwa.

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OPIS ROZPRAWY DOKTORSKIEJ

Autor rozprawy doktorskiej: mgr inż. Karolina Delińska

Tytuł rozprawy doktorskiej w języku polskim: Metoda opracowania uniwersalnej osnowy na bazie krzemionki do unieruchomienia cieczy jonowych jako materiałów sorpcyjnych w technice mikroekstrakcji do fazy stacjonarnej.

Tytuł rozprawy w języku angielskim: The development of universal silica-based matrix for the confinement of ionic liquids as sorption materials in the solid-phase microextraction technique.

Język rozprawy doktorskiej: polski

Promotor rozprawy doktorskiej: dr hab. inż. Adam Kloskowski

Data obrony:

Słowa kluczowe rozprawy doktorskiej w języku polskim: ciecze jonowe, technika mikroekstrakcji do fazy stacjonarnej, sorbenty porowate, zielona chemia analityczna, ekstrakcja, zanieczyszczenia organiczne

Słowa kluczowe rozprawy doktorskiej w języku angielskim: ionic liquids, solid-phase microextraction, porous sorbents, green analytical chemistry, extraction, organic pollutants

Streszczenie rozprawy w języku angielskim: The doctoral dissertation describes research conducted during the four years (2018-2022) of doctoral studies. The results of the research work have been published in the form of five original papers, which are the basis of this dissertation. The research subject concerns the use of ionic liquids in the solid-phase microextraction (SPME) technique. The main goal of the research was to obtain new, porous silica-based fiber coatings, immobilization of ionic liquids inside the pores of the obtained materials, and application of the fibers towards determination of the selected groups of analytes from water and food samples. In the conducted works, a new silica-based material was developed, with an appropriately selected precursor and pore-forming substance. The obtained sorption material was characterized by high chemical, thermal and mechanical stability. SPME fibers based on the developed sorption materials have been successfully used to isolate volatile and semi-volatile organic compounds from water and food samples. The analytes used in the research included compounds as benzene derivatives and organophosphorus insecticides. Optimization of the extraction conditions was carried out for the obtained fibers. During the last stage of the research, the extraction efficiency of the developed fibers was compared with commercial SPME fibers. The analysis of the obtained results showed that the developed sorption material, in the case of selected analytes in water and food samples, might be a real alternative to commercial solutions.

Streszczenie rozprawy w języku, w którym została napisana: Rozprawa doktorska stanowi opis badań prowadzonych w trakcie czterech lat (2018-2022) studiów doktoranckich. Rezultaty prac badawczych zostały opublikowane w postaci pięciu oryginalnych artykułów, stanowiących podstawę tej rozprawy. Tematyka badań dotyczy wykorzystania cieczy jonowych w technice mikroekstrakcji do fazy stacjonarnej (ang. SPME). Głównym celem prowadzonych prac

badawczych było: (a) otrzymanie nowej, porowatej sorpcyjnej powłoki włókna na bazie krzemionki, (b) unieruchomienie w porach otrzymanych materiałów cieczy jonowej oraz (c) wykorzystanie włókien w procesie ekstrakcji wybranych grup analitów z próbek wodnych oraz żywności. W toku prowadzonych prac opracowano nowy materiał sorpcyjny na bazie krzemionki, z odpowiednio dobranym prekursorem oraz substancją porotwórczą. Otrzymany materiał sorpcyjny charakteryzował się wysoką trwałością chemiczną, termiczną i mechaniczną. Włókna SPME na bazie opracowanych materiałów porowatych zostały z powodzeniem zastosowane w izolacji lotnych oraz średnio-lotnych związków organicznych. Anality, które zostały wykorzystane w przeprowadzonych badaniach obejmowały związki z grupy pochodnych benzenu oraz insektycydów organofosforowych. Z wykorzystaniem otrzymanych włókien przeprowadzono procedurę optymalizacji warunków prowadzenia ekstrakcji z fazy nadpowierzchniowej badanych próbek. Właściwości ekstrakcyjne opracowanych włókien porównano z właściwościami włókien komercyjnych. Analiza uzyskanych wyników wykazała, że opracowany materiał sorpcyjny, w przypadku wybranych analitów w próbkach wodnych żywnościowych oraz żywności, może stanowić rzeczywistą alternatywę wobec rozwiązań komercyjnych.

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PODZIĘKOWANIA

Dziękuję mojemu promotorowi dr hab. inż. Adamowi Kloskowskiemu za nieocenioną pomoc udzieloną w trakcie prowadzonych badań oraz przygotowywania pracy doktorskiej, cierpliwość i wyrozumiałość oraz motywację do krytycznego spojrzenia na problematykę badawczą. Dziękuję za pomoc w jasnym formułowaniu myśli naukowej oraz inspirację do zagłębiania zagadnień naukowych.

Serdeczne podziękowania dla mojego zespołu naukowego, dla dr hab. inż. Adama Kloskowskiego, dr inż. Łukasza Marcinkowskiego, dr inż. Pauliny Rakowskiej, dr inż. Kateryny Yavir i mgr inż. Joachima Eichenlaub za otrzymane wsparcie, pomoc i przyjazną atmosferę pracy. Mam nadzieję, że te przyjazne stosunki uda nam się utrzymać przez lata.

Dziękuję również wszystkim kolegom i współpracownikom z Katedry Chemii Fizycznej, a także kolegom i pracownikom Katedry Chemii Analitycznej oraz Organicznej Wydziału Chemicznego Politechniki Gdańskiej za pomoc i przyjazną atmosferę okazaną podczas studiów doktoranckich.

Dziękuję mężowi Patrykowi, rodzicom Małgorzacie i Stanisławowi, rodzeństwu Joannie i Wiktorowi za wsparcie, motywację i cierpliwość. Dziękuję Wam za nigdy niegasnącą wiarę we mnie.

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Spis treści

SKRÓTY I AKRONIMY

Akronim/skrót	Termin w j. angielskim	Termin w j. polskim
CAR	Carboxen	-
CW	Carbowax	-
D-SPME	Direct immersion - solid phase microextraction	Mikroekstrakcja do fazy stacjonarnej bezpośrednio z badanej próbki
DMF	Dimethyloformamid	Dimetyloformamid
DVB	Divinylbenzene	Diwinylobenzen
EF	Enrichment factor	Współczynnik wzbogacenia
GC	Gas chromatography	Chromatografia gazowa
HS-SPME	Headspace – solid phase microextraction	Mikroekstrakcja do fazy stacjonarnej z fazy nadpo-wierzchniowej badanej próbki
IL	Ionic liquid	Ciecz jonowa
LOD	Limit of detection	Granica wykrywalności
LOQ	Limit of quantification	Granica oznaczalności
LZO	Volatile Organic Compounds	Lotne Związki Organiczne
MIL	Magnetic ionic liquid	Magnetyczna ciecz jonowa
PA	Polyacrylate	Poliakrylan
PDMS	Polydimethylsiloxane	Polidimetylosiloksan
PEEK	Polyeteroeteroketone	Polieteroeteroketon
PEG	Polyethylene glycol	Glikol polietylenowy
PEO	Polyethylene oxide	Politlenek etylenu

PIL	Polymeric ionic liquid	Polimerowa ciecz jonowa
SEM	Scanning electron microscope	Skaningowy mikroskop elektronowy
SPME	Solid phase microextraction	Mikroekstrakcja do fazy stacjonarnej
TGA	Thermogravimetric analysis	Analiza termograwimetryczna
WWA	Polycyclic aromatic hydrocarbons	Wielopierścieniowe Węglowodory Aromatyczne

1. WSTĘP

W większości przypadków, analiza próbek środowiskowych wymaga, aby przed etapem oznaczeń końcowych wprowadzić do procedury analitycznej dodatkowy etap przygotowania próbki. Spośród istniejących technik przygotowania próbki do analizy, na szczególną uwagę zasługuje technika mikroekstrakcji do fazy stacjonarnej (Solid-phase microextraction - SPME). Proces ekstrakcji w technice SPME polega na umieszczeniu włókna pokrytego fazą sorpcyjną bezpośrednio w analizowanej próbce lub fazie gazowej pozostającej z nią w kontakcie [1]. Wydajność techniki SPME, ze względu na ograniczoną objętość fazy sorpcyjnej jest ściśle uzależniona od jej właściwości ekstrakcyjnych. W przypadku włókien komercyjnych, wybór materiału powłoki jest bardzo ograniczony. Materiały te można podzielić na dwie ogólne kategorie: dedykowane izolacji analitów niepolarnych oraz polarnych. W pierwszym przypadku, za najważniejszy materiał sorpcyjny należy uznać polidimetylosiloksan (PDMS), natomiast włókna dedykowane polarnym analitom bazują na stałych adsorbentach jak Carboxen czy Carbowax. Jest to o tyle istotne, ponieważ izolacja polarnych analitów z próbek wodnych lub rzeczywistych jest skomplikowanym zagadnieniem, ze względy na ich podobieństwo pod względem oddziaływań międzycząsteczkowych do matrycy próbki. W takiej sytuacji zastosowanie adsorbentów czyni procedurę ekstrakcji podatną na niekorzystne zjawisko adsorpcji konkurencyjnej, która w konsekwencji w zasadniczy sposób wpływa na ilościowy opis całego procesu [2]. Ograniczenia te są możliwe do wyeliminowania, jeśli zastosowane zostaną materiały w ciekłym lub

„pseudociekłym” stanie skupienia. Materiały te umożliwią izolację składników próbki poprzez mechanizm absorpcji (podziału). Problemem jest natomiast ich powinowactwo do matrycy próbek polarnych co może skutkować ich rozpuszczeniem. Jedną z grup substancji, które stanowią obiecującą alternatywę dla stałych pokryć włókien SPME, są ciecze jonowe. Dotychczasowy stan badań nad wykorzystaniem tej grupy substancji jako materiałów sorpcyjnych w technice SPME jest dość ograniczony z uwagi na brak skutecznych i powtarzalnych technik ich osadzania na włóknie urządzenia do SPME [3]. Ze względu na strukturę jonową, substancje te cechuje: pomijalnie niska prężność pary, wysoka stabilność termiczna, występowanie w fazie ciekłej w szerokim zakresie temperatur oraz powinowactwo do związków organicznych lub nieorganicznych. Ponadto, dzięki olbrzymich możliwości łączenia par kation-anion, ciecze jonowe mogą być uznane za jedną z najbardziej elastycznych grup związków chemicznych pod względem „kontrolowania” ich właściwości fizycznych i chemicznych (często nazywane „designer solvents”). Potencjał ten nie został jeszcze wykorzystany analizy technikach separacyjnych, a w tym w technice SPME. Kluczowym problem z zastosowaniem cieczy jonowych w technice SPME, jest niska stabilność oraz odtwarzalność metod wytwarzania warstwy cieczy jonowej na powierzchni włókna. W ostatnich latach podjęto kilka prób, w celu przezwyciężenia danego problemu. Jednymi z najbardziej obiecujących są prowadzone na Wydziale Chemicznym Politechniki Gdańskiej [4] badania dotyczące powlekania włókna do SPME z wykorzystaniem procesu przemiany ciekłego zolu w stały żel krzemionkowy, a także unieruchamianie cieczy jonowych poprzez ich polimeryzację (grupa prof. Andersona) [5]. Obie metody, jakkolwiek z różnych przyczyn, ze względy na charakter chemiczny zachodzących reakcji ograniczają wybór możliwych do zastosowania cieczy jonowych. Tym samym, nie pozwalają na swobodny dobór struktury chemicznej cieczy jonowej pod kątem wybranej grupy analitów lub próbek.

W celu przezwyciężenia omawianych problemów, zaproponowano utworzenie uniwersalnej - porowatej oraz stałej powłoki na powierzchni włókna SPME. Opracowana metoda syntezy i pokrycia włókna warstwą materiału porowatego powinna umożliwić powtarzalne otrzymywanie struktury o ściśle określonej średnicy i objętości porów. Porowaty materiał ma stanowić osnowę umożliwiającą unieruchomienie w swoich porach dowolnej cieczy jonowej - ciecz jonowa zostanie unieruchomiona za pomocą sił kapilarnych. Wszechstronność proponowanej matrycy będzie związana z unieruchomieniem różnych rodzajów cieczy jonowych, o różnym stopniu polarności. Zaletą proponowanego rozwiązania jest możliwość przeprowadzenia badań, dotyczących wykorzystania właściwości cieczy jonowych, które są bezpośrednio związane z ich strukturą chemiczną.

Rozprawa doktorska została napisana w oparciu o pięć oryginalnych publikacji. Dwie z nich, to publikacje przeglądowe:

- R. Marcinkowska, **K. Delińska (Konieczna)**, Ł. Marcinkowski, J. Namieśnik, A. Kloskowski, Application of ionic liquids in microextraction techniques: Current trends and future perspectives, TrAC Trends in Analytical Chemistry 119 (2019) 115614 – Załącznik 1.

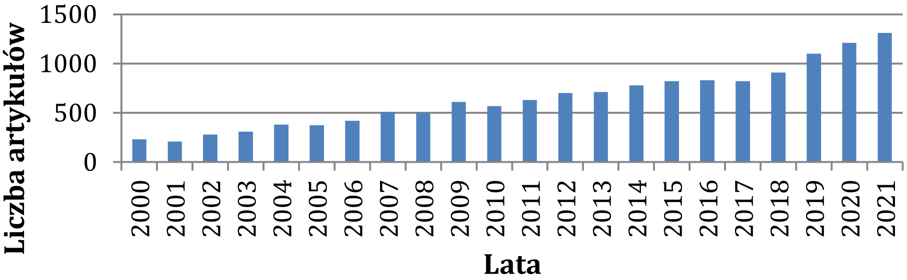
- **K. Delińska**, P. W. Rakowska, A. Kloskowski, Porous material-based sorbent coatings in solid-phase microextraction technique: Recent trends and future perspectives, TrAC Trends in Analytical Chemistry (2021) 143 116386 – Załącznik 2.

Wyniki przeprowadzonych badań zostały opisane w trzech pracach badawczych:

- **K. Delińska (Konieczna),** K. Yavir, M. Kermani, A. Mielewczyk-Gryń, A. Kloskowski, The new silica-based coated SPME fiber as universal support for the confinement of ionic liquid as an extraction medium, Separation and Purification Technology (2020) 252, 117411 – Załącznik 3.
- **K. Delińska**, G. Machowski, A. Kloskowski, Development of SPME fiber coatings with tunable porosity for physical confinement of ionic liquids as an extraction media, Microchemical Journal (2022) 107392 – Załącznik 4.
- **K. Delińska**, K. Yavir, A. Kloskowski, Head space for the analysis of organophosphorous insecticides by silica IL-based fibers in real samples, Molecules (2022) – Załącznik 5.

1.1. TECHNIKA MIKROEKSTRAKCJI DO FAZY STACJONARNEJ

Od czasu wynalezienia techniki SPME liczne zespoły badawcze skupiły się na szeroko rozumianym rozwoju techniki. W efekcie, corocznie publikowanych jest szereg artykułów naukowych z tego zakresu (Rys. 1), co wskazuje na znaczną popularność techniki SPME w świecie naukowym.

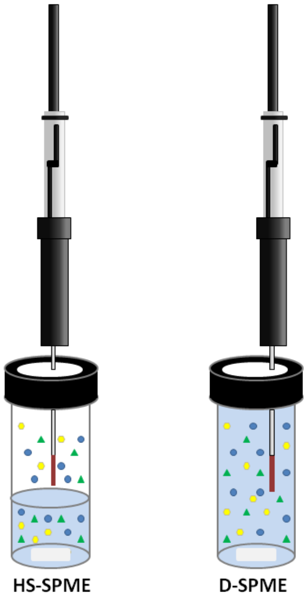


Rysunek 1. Liczba artykułów opisujących zastosowanie SPME (Baza danych *Scopus*, 2021; słowa kluczowe: technika mikroekstrakcji do fazy stacjonarnej, *ang. solid-phase microextraction*).

Jak już wspomniano, oznaczanie analitów obecnych na poziomie śladowym i ultra-śladowym w próbkach ze złożonym składem matrycy pełni niezwykle ważną rolę w ocenie oraz monitorowaniu środowiska, natomiast liczba odpowiednio czułych technik analitycznych, służących bezpośredniemu oznaczaniu składników obecnych w próbce w ilościach śladowych jest ograniczona, co wiąże się z koniecznością przeprowadzenia wstępnego etapu izolacji/wzbogacenia analitu przed dokonaniem oznaczeń końcowych. Etap ten posiada istotne znaczenie w odniesieniu do dokładności oraz wiarygodności wyników całej procedury analitycznej. W ostatnich latach, pojawiły się dodatkowe okoliczności, które wynikają z zasad Zielonej Chemii Analitycznej [6], które muszą być wzięte pod uwagę i które tym samym, stanowią podstawę rozwoju nowych rozwiązań metodologicznych i technicznych. Do najbardziej podstawowych wymagań należą: zminimalizowana ilość wytwarzanych odpadów, a także stosowanie bezpiecznych, nietoksycznych odczynników oraz mediów ekstrakcyjnych. Jedną z najpopularniejszych technik przygotowania próbek do analizy, która spełnia wymagania Zielonej Chemii Analitycznej jest mikroekstrakcja do fazy stacjonarnej (SPME), która została opracowana w latach 90. Przez prof. Janusza Pawliszyna [7]. Technika ta znalazła zastosowanie do pobierania szerokiego spektrum analitów z mediów gazowych, ciekłych oraz stałych, o zróżnicowanym składzie matrycy. Ogromna popularność techniki SPME wynika z jej niewątpliwych zalet: prostoty obsługi, krótkiego czasu ekstrakcji, bezrozpuszczalnikowego charakteru procesu, a także możliwości pełnej automatyzacji. Dodatkowo, próbki mogą zostać pobrane in-situ, a wiarygodne wyniki uzyskuje się dla analitów obecnych w ilościach śladowych. Niemniej jednak, technika SPME nie jest pozbawiona wad: niska selektywność, a także ograniczone możliwości wyboru odpowiedniego włókna ekstrakcyjnego [8].

Typowe urządzenie SPME składa się z rdzenia pokrytego cienką warstwą odpowiedniego (ad)sorbentu. Włókno jest umieszczone wewnątrz igły uchwytu podobnego do strzykawki. Ekstrakcję można przeprowadzić poprzez ekspozycję włókna w fazie gazowej lub odpowiednio czystej próbki ciekłej (DI-SPME – direct immersion-solid phase microextraction) oraz z fazy nad powierzchniowej próbki ciekłej lub stałej (HS-SPME – headspace-solid phase microextraction) [9] (Rys. 2).

Wydajność SPME ze względu na ograniczoną objętość fazy ekstrakcyjnej (<1μL) zależy od doboru odpowiedniego materiału powłoki, zapewniającego wysokie powinowactwo do wskazanych analitów. W praktyce, wybór pokryć włókien SPME jest ograniczony polidimetylosiloksanu (PDMS), diwinylbenzenu (DVB), poliakrylanu (PA), Carboxenu (CAR) oraz glikolu polietylenowego (PEG, Carbowax, CW), dostępnych w różnych grubościach oraz kombinacjach [10].



Rysunek 2. Schemat ekstrakcji analitu przy użyciu techniki HS-SPME i DI-SPME.

Rodzaj zastosowanej fazy ekstrakcyjnej określa polarność powłoki. Powłoki SPME można podzielić według trzech kryteriów: grubości powłoki, jej polarności oraz według tego, czy powłoka jest absorbentem lub adsorbentem. Dostępne rodzaje włókien komercyjnych nie są w stanie zapewnić optymalnych właściwości sorpcyjnych dla wielu różnych kombinacji analit-matryca [11]. Z tego powodu, przez ostatnie dwie dekady główny kierunek rozwoju SPME dotyczył nowatorskich materiałów powłokowych, które można wykorzystać do produkcji włókna SPME. Naukowcy szukali materiałów o wysokim powinowactwie do wybranych analitów [12]. Obecnie dostępne oraz stosowane do tej pory materiały sorpcyjne, wykorzystywane w SPME, a także cieszące się największą popularnością to: nanocząstki metali szlachetnych [13], sorbenty na bazie krzemionki (ditlenek krzemu) [14], polimery molekularnie wdrukowane [15], polimery przewodzące [16], oparte na sorbentach węglowych jak nanorurki węglowe [17] i grafen [18]. Powłoki adsorpcyjne wiążą anality zwykle przez silne i specyficzne oddziaływania międzycząsteczkowe. Grupy funkcyjne (miejsca aktywne) zlokalizowane na powierzchni adsorbentu mogą oddziaływać z analitem, za pomocą wiązań π-π, wodorowych lub oddziaływań van der Waalsa. Biorąc pod uwagę sposób, w jaki anality są unieruchomione na powierzchni adsorbentu, ważne jest, aby wziąć pod uwagę podstawy termodynamiczne procesu adsorpcji analitów.

W celu ilościowego opisu procesu ekstrakcji, wykorzystywane jest pojęcie stopnia pokrycia θ, który można opisać za pomocą zależności:

$$\theta = \frac{C_{ads}^{a}}{C_{ads}} \qquad (1)$$

gdzie:

C_{ads}^{a} stężenie zaadsorbowanego analitu w przeliczeniu na objętość ekstrahenta [mol·dm^{-3}];

C_{ads}- całkowite stężenie liczby miejsc aktywnych wyrażone w przeliczeniu na objętości ekstrahenta [mol·dm^{-3}].

Powyższy zapis równania (1) jest słuszny przy założeniu, że rozkład miejsc aktywnych na powierzchni adsorbenta jest jednorodny. Jeżeli do opisu procesu adsorpcji analitu na powierzchni adsorbenta wykorzystany zostanie model izotermy Langmuira w następującej postaci:

$$\theta = \frac{K_{ads/p}\, C_{p,eq}}{1+K_{ads/p}\, C_{p,eq}} \qquad (2)$$

gdzie: $K_{ads/p}$ - stała równowagi adsorpcji (współczynnik podziału),wówczas po podstawieniu do równania (2) zależności opisanej równaniem (1) otrzymuje się zależność wiążącą stężenie analitu na powierzchni adsorbenta w funkcji współczynnika podziału $K_{ads/p}$ w stanie równowagi:

$$C_{ads}^{a} = C_{ads} \frac{K_{e/p}\, C_{p,eq}}{1+ K_{e/p}\;\; C_{p,eq}} \qquad (3)$$

W oparciu o analizę powyższego równania możliwe jest wyciagnięcie kilku istotnych wniosków:

- stężenie zaadsorbowanego analitu jest nieliniową funkcją jego stężenia w próbce (ma to istotny wpływ na wyznaczanie krzywej kalibracyjnej),
- liniowy charakter zależności (3) można osiągnąć jedynie w sytuacji, gdy wartość iloczynu $K_{e/p} \cdot C_{p,eq}$ jest dużo mniejsza od jedności. Jednakże, dotyczy to jedynie sytuacji gdy analit występuje na bardzo niskich poziomach stężeń lub wykazuje znikome powinowactwo do adsorbenta, co jest sytuacją nieracjonalną.

W konsekwencji, proces izolacji/wzbogacania lub inaczej pobierania próbek analitów oparty na wykorzystaniu materiałów stałych, które bazują na mechanizmie adsorpcji cechuje istotne ograniczenie zakresu liniowości w porównaniu do przebiegu tego samego procesu opartego na mechanizmie podziałowym czyli absorpcji.

Kolejnym istotnym aspektem mogącym ograniczyć stosowanie adsorbentów jako faz stacjonarnych w technice SPME, jest zrozumienie właściwości powierzchni aktywnej adsorbenta opisywanej za pomocą C_{ads}. Parametr ten, w równaniu (3) charakteryzuje liczbę dostępnych miejsc aktywnych jedynie w odniesieniu do jednego rodzaju analitu. Jakkolwiek całkowita liczba miejsc aktywnych dostępnych dla cząsteczki analitu na powierzchni adsorbenta jest stała, to zależy ona również od powinowactwa adsorbenta do innych składników próbki. Innymi słowy, w przypadku próbek o złożonym składzie możliwe jest zajście zjawiska konkurowania analitów z pozostałymi składnikami próbki o dostępne miejsca aktywne na powierzchni adsorbenta. Składniki o dużym powinowactwie do powierzchni adsorbenta lub występujące w próbce na wysokim poziomie stężeń zajmują dostępne miejsca na powierzchni materiału stałego. W konsekwencji, prowadzi to do ograniczenia zarówno maksymalnej ilości analitów, jaka może zostać unieruchomiona na powierzchni adsorbenta w stanie równowagi, jak również dochodzi do zmniejszenia się zakresu liniowości procesu ekstrakcji.

2. CIECZE JONOWE

Ciecze jonowe *(ang. ionic liquids)* są definiowane jako związki złożone wyłącznie z jonów, które charakteryzują się temperaturą topnienia poniżej 100°C [19-20]. Właściwość ta jest zazwyczaj rezultatem znaczącej różnicy w rozmiarach organicznego kationu o rozbudowanej, asymetrycznej strukturze i niewielkiego anionu organicznego lub nieorganicznego.

Pierwszą opisaną w literaturze cieczą jonową był azotan etyloamoniowy, o temperaturze topnienia poniżej temperatury pokojowej (12°C), otrzymany przez Paula Waldena w 1914 roku [21]. Niestety, w latach 50 – 90 XX w. zainteresowanie cieczami jonowymi wśród naukowców nie zyskało szczególnej popularności w prowadzonych przez nich badaniach [22-25]. Wzrost zainteresowania tematyką cieczy jonowych został zaobserwowany w ciągu ostatnich dwóch dekad, co jest wynikiem prac, które były rezultatem syntezy pierwszych cieczy jonowych, stabilnych w kontakcie z wilgocią i powietrzem, opartych na kationie imidazoliowym [26].

Ciecze jonowe dość szybko zaczęły być określane jako „zielona" alternatywa dla popularnych rozpuszczalników organicznych. Naukowcy chętniej wykorzystywali w swoich badaniach ciecze jonowe, z uwagi na, jak początkowo sądzono, ich przyjazny wobec środowiska naturalnego charakter, a jednocześnie doceniali ich unikalną zaletę, jaką jest projektowalność *(ang. designer solvents)*. Zaleta ta umożliwia naukowcom, poprzez dobór odpowiedniego kationu lub anionu, zaprojektowanie cieczy jonowej o pożądanych właściwościach [27].

Wśród najbardziej popularnych kationów cieczy jonowych można wymienić kation: imidazoliowy, pyridinowy, pyrolidinowy, fosfoniowy, amoniowy i siarkowy. Do najpowszechniej wykorzystywanych anionów należą: heksafluorofosforan, tetrafluoroboran, siarczan alkilu, metanosulfonian, bis(trifluoromethylsulfonylo)imid oraz halogenki. Obecny stan wiedzy, dotyczący struktury chemicznej cieczy jonowych, ich właściwości oraz ich możliwych zastosowań w różnych dziedzinach umożliwia dokonanie ich podziału na trzy generacje:

- ciecze jonowe z unikalnymi właściwościami fizycznymi;
- ciecze jonowe z wybranymi właściwościami fizycznymi oraz pożądanymi właściwościami chemicznymi;
- ciecze jonowe z wybranymi właściwościami fizyko-chemicznymi oraz pożądanej aktywności biologicznej.

Równolegle z tradycyjnymi cieczami jonowymi, powstają nowe podklasy cieczy jonowych, takie jak polimerowe ciecze jonowe *(ang. PILs)* [28-30] oraz magnetyczne ciecze jonowe *(ang. MILs)* [31-32]. Struktura cieczy jonowych odpowiada za ich wyjątkowe właściwości fizyczne i mechaniczne.

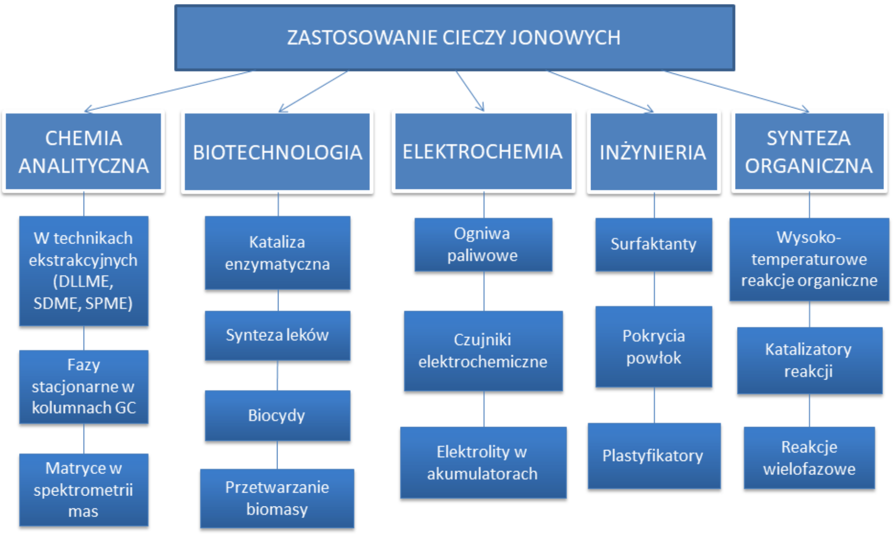
Do najważniejszych właściwości cieczy jonowych zaliczane są:

- wysoka stabilność termiczna,
- niska temperatura topnienia (stan ciekły w szerokim zakresie temperatur),
- pomijalnie niska prężność pary,
- powinowactwo do związków organicznych i nieorganicznych,

- wysoka przewodność jonowa i cieplna,
- wysoka lepkość i gęstość,
- możliwość zaprojektowania cieczy jonowych w oparciu o ogromną liczbę kombinacji kationów i anionów.

Ostatnia z wymienionych właściwości to zasadnicza przewaga cieczy jonowych nad innymi substancjami. Przy prawidłowym doborze kationu, anionu oraz długości podstawnika alkilowego łańcucha można zaprojektować lub poprawić właściwości cieczy jonowych wobec wybranego zastosowania. W związku z tym, badanie natury cieczy jonowych, wpływu różnych kationów i anionów na ich właściwości, a także znajdowanie zależności i ich wyjaśnianie jest podstawowym zadaniem służącym lepszemu zrozumieniu zależności między strukturą i właściwościami cieczy jonowych, tym samym, rozszerzając zakres możliwości ich zastosowania. Wymienione kwestie zostały dokładnie przeanalizowane i omówione w artykule przeglądowym (Załącznik 1).

Obecnie, ciecze jonowe znajdują szerokie zastosowanie w różnych dziedzinach nauki i techniki. Rysunek 3. przedstawia schemat ideowy z najpopularniejszymi obszarami zastosowań cieczy jonowych. Głównym celem prowadzonych badań było zastosowanie cieczy jonowych w technice mikroekstrakcji do fazy stałej.



Rysunek 3. Zastosowania cieczy jonowych.

2.1. WYKORZYSTANIE CIECZY JONOWYCH I MATERIAŁÓW POROWATYCH W TECHNICE SPME

Pierwsze próby powlekania włókna SPME za pomocą cieczy jonowych zostały przeprowadzone w 2005 r. [33], jednakże, uzyskane włókna mogły być użyte tylko jednokrotnie, wymagając ponownego powlekania, po każdej przeprowadzonej ekstrakcji. Ponadto, niska wydajność izolacji analitów, ze względu na cienką warstwę ekstrakcyjną stanowi kolejną, niekorzystną cechę proponowanego rozwiązania. W celu częściowego złagodzenia przedstawionego problemu, w kolejnej pracy włókno najpierw zostało pokryte cienką warstwą polimeru Nafion, a następnie cieczą jonową [34]. Polimer zwiększył zwilżalność powierzchni, a zatem umożliwił utworzenie grubszej warstwy cieczy jonowej. Włókno to zostało wykorzystane w SPME do ekstrakcji wielopierścieniowych węglowodorów aromatycznych (WWA) z próbek wodnych. Niestety, po przeprowadzeniu analizy, za każdym razem wymagane było zmycie warstwy sorbentu i ponowne powlekanie włókna, co poważnie ogranicza praktyczne zastosowanie tej techniki. Problemy związane z niską trwałością włókien pokrytych cieczami jonowymi zostały wyeliminowane poprzez wprowadzenie polimerowych cieczy jonowych [35]. Związki te charakteryzują się wysoką stabilnością termiczną, pozwalając na długotrwałe użytkowanie włókna (nawet do 150 ekstrakcji), bez konieczności ponownego powlekania fazą stacjonarną. Kolejne propozycje to impregnacja za pomocą cieczy jonowych elastomerów silikonowych [36], wykorzystanie techniki metodą zol-żel [37], a także sieciowania in-situ na włóknach ze stali nierdzewnej, pokrytych mikrostrukturowym srebrem [38].

Kolejne, bardzo obiecujące podejście zostało zaproponowane przez zespół prof. J. Namieśnika i dr A. Kloskowskiego [39]. Tym razem, ciecz jonowa została unieruchomiona w sieci krzemionkowej w postaci jonożelu. Otrzymane włókna charakteryzowały się wysoką trwałością, podczas gdy unieruchomiona ciecz jonowa utrzymywała stan ciekły. Przedstawiona procedura syntezy powłok dla SPME, opartych na jonożelu jest skomplikowana i trudna do odtworzenia. Dodatkowo, za każdym razem, gdy pojawia się zastosowanie nowej cieczy jonowej, wymagana jest optymalizacja parametrów syntezy jonożelu. Podsumowując, w celu pełnego zbadania potencjału cieczy jonowych jako faz stacjonarnych w technice SPME, istnieje potrzeba opracowania metody unieruchomienia cieczy jonowej na powierzchni włókna, w sposób, który umożliwi utworzenie warstwy stabilnej zarówno mechanicznie, jak i termicznie, przy jednoczesnym zachowaniu stanu ciekłego unieruchomionej cieczy jonowej.

Rozwój w dziedzinie produkcji nowych włókien SPME, opartych na wykorzystaniu cieczy jonowych jest ograniczony, ze względu na słabą trwałość warstwy cieczy jonowej na powierzchni włókna. Polimerowe ciecze jonowe można uznać za rozwiązanie omawianego problemu, ponieważ charakteryzują się one wysoką trwałością, jednakże, forma spolimeryzowana nie zachowuje właściwości fizykochemicznych wyjściowych cieczy jonowych, co utrudnia możliwości przewidywania ich właściwości ekstrakcyjnych. Dodatkowo, ograniczony jest wybór cieczy jonowych, jedynie do tych, które mogą ulegać reakcji polimeryzacji. Opracowanie metody otrzymania trwałej struktury porowatej na powierzchni włókna pozwoli na uzyskanie uniwersalnej, stałej sieci, w celu unieruchomienia praktycznie każdej cieczy jonowej, jednocześnie zachowując jej ciekły stan oraz oryginalne właściwości. Zastosowanie cieczy jonowych unieruchomionych w materiałach porowatych jako sorbentów w technice SPME wymaga opracowania odpowiednio wytrzymałego materiału, który zostanie pomyślnie wykorzystany w zmiennych warunkach. Głębsze zrozumienie natury nowo opracowanych porowatych powłok SPME oraz wpływ ich struktur na parametry analityczne ma kluczowe znaczenie dla zapewnienia ich pomyślnego wykorzystania.

Właściwości fizykochemiczne powłok ekstrakcyjnych na bazie materiałów porowatych w mikroekstrakcji do fazy stacjonarnej, wraz z ich poszczególnymi zastosowaniami zostały szczegółowo omówione w artykule przeglądowym (Załącznik 2).

3. CELE BADAWCZE

Badania przeprowadzona w trakcie realizacji pracy doktorskiej były ukierunkowane na opracowanie metody służącej do utworzenia trwałej warstwy porowatego materiału na powierzchni włókna SPME. Celem było unieruchomienie potencjalnie każdej cieczy jonowej, w porach otrzymanego materiału, przy jednoczesnym zapewnieniu przydatnego narzędzia analitycznego, które będzie użyte w etapie przygotowania próbki do analizy. Podstawowym celem badawczym było opracowanie powtarzalnej technologii nanoszenia materiału porowatego, który spełniałby kilka kryteriów: powinien być materiałem o wysokiej stabilności mechanicznej oraz termicznej, powinien cechować się niewielkim powinowactwem do docelowej grupy analitów, wielkość oraz objętość porów powinna umożliwić wysoki stopień wypełnienia materiału porowatego cieczą jonową oraz zapewnić jej fizyczne unieruchomienie. Proponowane rozwiązanie stworzy możliwość prowadzenia szeroko zakrojonych badań związanych z doborem cieczy jonowej optymalnej dla danej grupy analitów i/lub próbek. Możliwość wykorzystania cieczy jonowych bez konieczności ich modyfikacji chemicznej, np. wskutek polimeryzacji, może stać się podstawą do szeroko zakrojonych i systematycznych badań dotyczących wpływu struktury chemicznej na właściwości ekstrakcyjne.

Realizacja badań prowadzonych w ramach Studium Doktoranckiego wymagała realizacji następujących celów badawczych:

- opracowania procedury otrzymywania materiałów sorpcyjnych na bazie krzemionki;

- opracowania techniki pokrywania włókna szklanego i metalowego powłoką krzemionki;
- opracowania metodyki unieruchomienia cieczy jonowych w porach materiału włókna;
- zbadania mechanizmu ekstrakcji z zastosowaniem wodnych roztworów modelowych zwierających testowy zestaw związków z grupy Lotnych Związków Organicznych (LZO), jako związków testowych;
- weryfikacji praktycznej uzyskanych powłok ekstrakcyjnych w zastosowaniu do izolacji insektycydów z próbek wodnych oraz żywności, a w tym:
  - optymalizacji parametrów ekstrakcji SPME;
  - walidacji opracowanej metody;
  - oceny wpływu efektu matrycy.

4. PRZEBIEG PRAC BADAWCZYCH

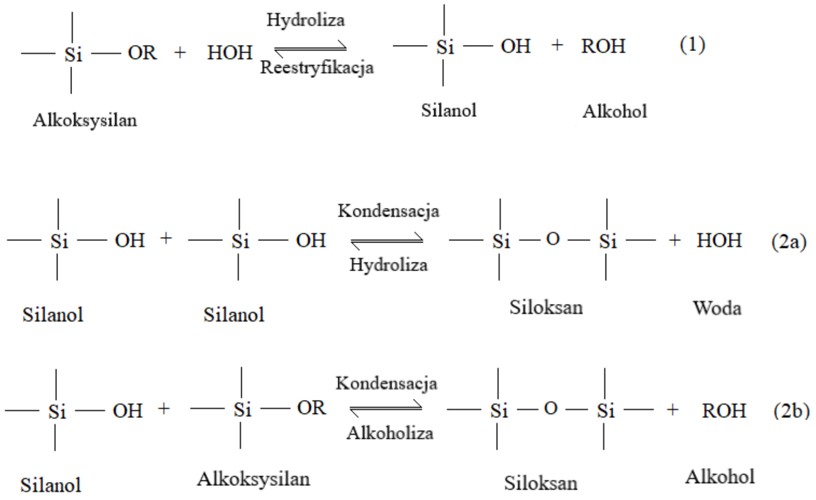
4.1. OTRZYMYWANIE MATERIAŁU POROWATEGO

W oparciu o dostępne dane literaturowe zdecydowano, że materiał porowaty będzie stanowić odpowiednio spreparowana sieć krzemionkowa. Podstawowymi czynnikami, które zdecydowały o wyborze, była zbadana wcześniej neutralność sieci krzemionkowej w odniesieniu do szerokiej gamy analitów o zróżnicowanej polarności [40]; wysoka wytrzymałość termiczna i mechaniczna oraz szeroka gama parametrów pozwalających na uzyskiwanie materiału porowatego o bardzo zróżnicowanych wartościach rozmiarów i objętości porów. Do liczby parametrów decydujących o końcowym efekcie należy zaliczyć przede wszystkim: dobór odpowiedniego prekursora krzemionki, dobór rodzaju i ilości porogenu oraz modyfikacja parametrów prowadzenia wieloetapowego procesu żelowania i kondycjonowania materiału. Pierwsze badania poświęcone opracowaniu metodyki otrzymywania krzemionkowego materiału porowatego zostały przeprowadzone w 2020 roku [41]. Pierwszym krokiem przeprowadzonych eksperymentów było zbadanie właściwości materiałów porowatych w zależności od wybranego prekursora, którymi były odpowiednio krzemian sodu (Na_2SiO_3) i krzemian potasu (K_2SiO_3). We wszystkich przeprowadzonych eksperymentach, jako środek porotwórczy, użyty został dimetyloformamid (C_3H_7NO). Syntezę materiałów krzemionkowych przeprowadzono w dwuetapowym procesie zol-żel (Rys. 4), przebiegający zgodnie z następującymi reakcjami:

Hydroliza: $Na_2SiO_3 + H_2O + 2HCl \rightarrow Si(OH)_4 + 2NaCl$ (1)

$K_2SiO_3 + H_2O + 2HCl \rightarrow Si(OH)_4 + 2KCl$ (2a)

Kondensacja: $Si(OH)_4 + (OH)_4Si \rightarrow (OH)_3Si - O - Si(OH)_3 + H_2O$ (2b)

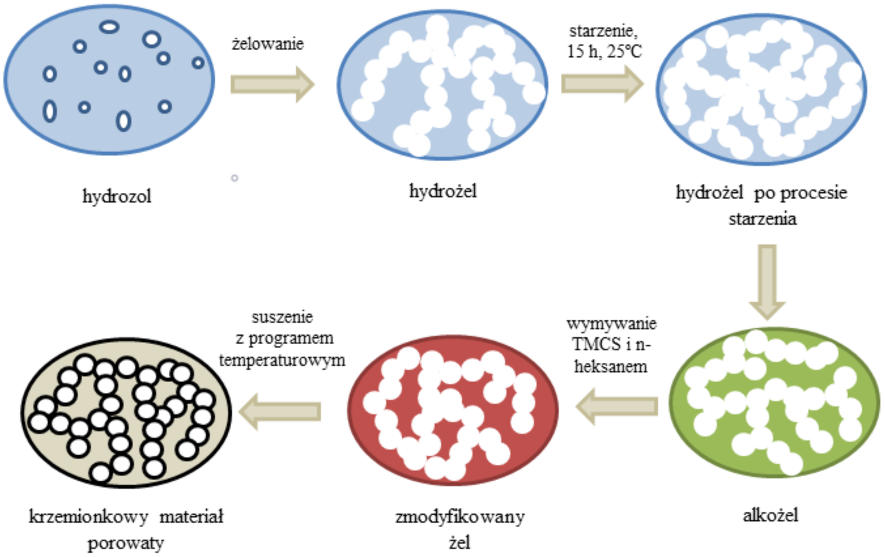


Rysunek 4. Schemat ideowy reakcji chemicznych syntezy zol-żel.

Równolegle, opracowano optymalne warunki przygotowania włókna szklanego służącego jako nośnik właściwej powłoki krzemionkowej. Przygotowanie włókna szklanego miało na celu wprowadzenie na powierzchnię szkła grup hydroksylowych, które umożliwiłyby chemiczne związanie powłoki z podłożem.

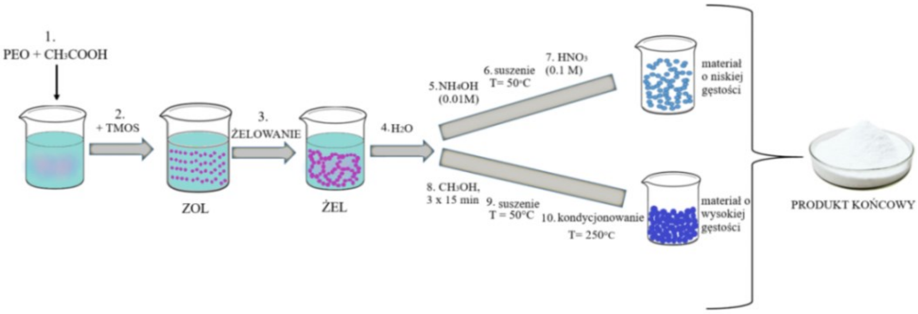
Oczekiwanym efektem modyfikacji powinno być silniejsze związanie powłoki ze szklanym włóknem, a tym samym, uzyskanie włókna o zwiększonej stabilności mechanicznej. W celu modyfikacji powierzchni, w przeprowadzonych eksperymentach zastosowano tzw. piranian kwasowy (kwas nadtlenosiarczanowy, 1:3 (v/v) H_2O_2:H_2SO_4) oraz NaOH. Na etapie optymalizacji, włókno szklane było wystawione na działanie mieszaniny reakcyjnej (trawieniu) przez 15, 30, 45 i 60 sekund. Badając siłę przyczepności powłoki do powierzchni, stwierdzono, że zwiększenie długości ekspozycji włókna zwiększa przyczepność powłoki do powierzchni szkła. Stwierdzono jednak, że zbyt długa ekspozycja znacznie osłabiła strukturę włókna szklanego, uniemożliwiając jego praktyczne wykorzystanie. Ostatecznie, optymalny czas trawienia powierzchni wynosił 30 sekund.

Ze względu na stosunkowo dużą lepkość, wyjściowy roztwór krzemianu sodu rozcieńczono wstępnie wodą destylowaną (objętościowo, w stosunku 2:1). Aby uzyskać jednorodny roztwór, odczynniki zostały poddane wstępnemu mieszaniu w probówce Eppendorf. Po wymieszaniu, które trwało 10 min, otrzymany roztwór wstrzyknięto strzykawką do rurki z materiału polimerowego (PEEK – polieteroeteroketon). Dno probówki PEEK zostało zamknięte septą, aby zapobiec wyciekowi roztworu zolu, natomiast wcześniej przygotowane włókno szklane zostało umieszczone wewnątrz rurki tak, aby możliwe było zamknięcie również jej górnej części. Cały system umieszczono w zamkniętej probówce Eppendorf. Po żelowaniu włókno zostało wyjęte z rurki PEEK i poddane kolejnym etapom procedury, jak pokazano na Rys. 5. Dokładny przebieg badań został opisany w pracach badawczych Załącznik nr 3 i 4.



Rysunek 5. Schemat procedury eksperymentalnej syntezy porowatego materiału krzemionkowego.

W celu rozszerzenia możliwości zastosowania opracowanej metody otrzymywania materiału porowatego, w ramach prowadzonych prac badawczych zaproponowano uzyskanie materiału porowatego z nowych substancji porotwórczych oraz prekursorów (Załącznik 4). Syntezę nowego materiału porowatego przeprowadzono analogicznie, jak w przypadku wcześniej wymienionych reagentów, w dwuetapowym procesie zol-żel (Rys. 6). Odczynniki zastosowane w omawianej reakcji to politlenek etylenu (PEO 20 kDa) jako substancja porotwórcza oraz tetrametyloortokrzemian (TMOS), jako prekursor. Wymienione odczynniki zostały wstępnie zmieszane w probówce Eppendorf, w celu uzyskania jednorodnego roztworu. Po wymieszaniu, roztwór pozostawiono do żelowania. Ze względu na dwie metodyki otrzymywania porowatego materiału krzemionkowego, poszczególne etapy obu syntez przedstawiono oddzielnie na Rys. 6. Obie procedury różniły się obecnością (górna droga) lub brakiem (dolna droga) etapów 5, 6 i 7.



Rysunek 6. Procedura syntezy zol-żel z wykorzystaniem TMOS jako prekursora i PEO jako substancji porotwórczej.

Próbki przygotowano przy zachowaniu stałego stosunku objętościowego TMOS i CH_3COOH, przy czym zastosowane roztwory kwasu octowego różniły się stężeniami. W badaniach użyto kwas octowy jako katalizator reakcji. Pierwszy etap syntezy materiału krzemionkowego polegał na rozpuszczeniu PEO (20 kDa) w kwasie octowym. Etap ten trwał około 10 minut. Temperaturę roztworu PEO (20 kDa) z kwasem octowym obniżono do 0°C, aż do uzyskania jednorodnej mieszaniny. Po osiągnięciu wymaganej temperatury, do roztworu dodano TMOS. Obniżenie temperatury było wymagane, ze względu na długi proces rozpuszczania TMOS. W obniżonej temperaturze hydroliza TMOS zostaje praktycznie zatrzymana, co pozwala na lepszą kontrolę kinetyki układu reakcji. Roztwór był mieszany aż do momentu otrzymania jednorodnej mieszaniny (ok. 1 godz.). Zgodnie ze schematem przedstawionym na Rys. 6, kolejnym etapem otrzymywania materiału porowatego było żelowanie roztworów, co osiągnięto poprzez podwyższenie temperatury do 50°C. Proces żelowania materiału prowadzono przez 24 godziny, w zamkniętych szklanych naczyniach. Po etapie żelowania próbki materiał poddano ocenie wizualnej, w kontekście koloru żelu, jego przezroczystości oraz twardości próbki (wytrzymałość mechaniczna). W przedstawionym wariancie otrzymywania porowatego materiału krzemionkowego z PEO (20 kDa) i TMOS jako podstawę włókna do SPME użyto odpowiednio przygotowanego chemicznie drutu ze stali nierdzewnej [42-43]. Drut ze stali nierdzewnej został przemyty metanolem, w celu usunięcia zanieczyszczeń organicznych, a następnie przemyty ultraczystą wodą. W kolejnym etapie, oczyszczony drut ze stali nierdzewnej (o długości 15 mm) został wytrawiony w 40% kwasie fluorowodorowym (HF), przez 5 minut w temperaturze 40°C.

Następnie, wytrawiony drut ze stali nierdzewnej przemyto ultraczystą wodą i zanurzono w kwasie chlorozłotowym ($HAuCl_4$) o stężeniu 2% (wag.), w celu chemicznego osadzania warstwy złota (Au) na powierzchni wytrawionego drutu ze stali nierdzewnej przez 30 minut w 30°C. Kolejno, wytworzone włókna spłukano ultraczystą wodą i osuszono na powietrzu. Następnie, włókna zanurzono w etanolowym roztworze 1mM 3-merkaptopropylotrietoksysilanu, przez 60 minut w temperaturze pokojowej. Nadmiar roztworu usunięto. W kolejnym etapie, włókna przemyto etanolem i ultraczystą wodą, a następnie wytworzone włókna zanurzono w mieszaninie powłokowej na bazie krzemionki. Mieszanina została przygotowana zgodnie z wcześniej opisaną procedurą.

Końcowym etapem otrzymywania włókna było jego kondycjonowanie w dozowniku GC, w temperaturze 220°C, do momentu uzyskania stabilnej linii sygnału detektora.

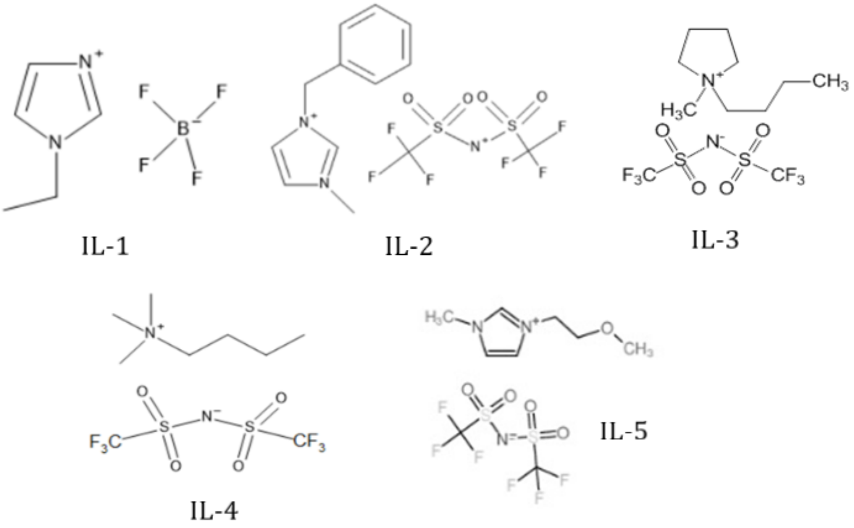
Przeprowadzona analiza otrzymanych materiałów krzemionkowych w kontekście ich wytrzymałości mechanicznej i termicznej oraz możliwości ekstrakcyjnych wykazała, że do kolejnych badań zdecydowano wykorzystać wariant przygotowany z materiałów K_2SiO_3 i FA.

4.2. WYBÓR I UNIERUCHOMIENIE CIECZY JONOWYCH W MATERIALE

Oprócz opracowania metody unieruchomienia cieczy jonowej na powierzchni włókna, za pomocą sposobu, który umożliwi utworzenie warstwy stabilnej zarówno mechanicznie, jak i termicznie, przy jednoczesnym zachowaniu stanu ciekłego unieruchomionej cieczy jonowej, równie istotny jest wybór odpowiedniej cieczy jonowej, która umożliwi osiągnięcie odpowiedniej selektywności oraz powinowactwa wobec konkretnych analitów. Jednocześnie, ciecz jonowa uznawana za materiał sorpcyjny dla włókna SPME musi spełniać takie wymagania jak: wysoka stabilność termiczna (powyżej 280-300°C dla termicznej desorpcji analitów w porcie iniekcyjnym GC), niska rozpuszczalność w wodzie oraz niska lepkość.

W przeprowadzonych badaniach wykorzystano pięć różnych cieczy jonowych. Do włókien wykonanych z materiału K_2SiO_3 oraz DMF wybrano jako modelową ciecz jonową tetrafluoroboran 1-etylo-3-metyloimidazoliowy (IL-1) (Załącznik 3); w badaniach z wykorzystaniem materiału TMOS i PEO (20 kDa) oraz K_2SiO_3 i FA do unieruchomienia wybrano ciecz jonową bis(trifluorometylosulfonylo)imid 1-benzylo-3-metyloimidazoliowy (IL-2) (Załącznik 4); natomiast w badaniach dotyczących oceny możliwości ekstrakcyjnych otrzymanych włókien w próbkach rzeczywistych, w celach porównawczych wybrano następujące, cztery ciecze jonowe: bis(trifluorometylosulfonylo)imid 1-benzylo-3-metyloimidazoliowy (IL-2) bis(trifluorometylosulfonylo)imid 1-butylo-1-metylopirolidyniowy (IL-3), bis(trifluorometylosulfonylo)imid butylotrimetyloamoniowy (IL-4) oraz bis(trifluorometylosulfonylo)imid 1-(2-metoksyetylo)-3-metyloimidazoliowy (IL-5) (Załącznik 5). W dalszej części pracy nazwy cieczy jonowych będą używane jako wskazane w tekście akronimy, nadane konkretnej cieczy jonowej.

Wyboru dokonano w oparciu o dostępne dane literaturowe dotyczące stabilności termicznej oraz wysokiej hydrofobowości anionu [44-46]. Wybrane parametry fizykochemiczne oraz struktury chemiczne cieczy jonowych wykorzystywanych w dalszych badaniach przedstawiono odpowiednio na Rys. 7 w Tabeli 1.



Rysunek 7. Struktury chemiczne cieczy jonowych wykorzystanych w badaniach.

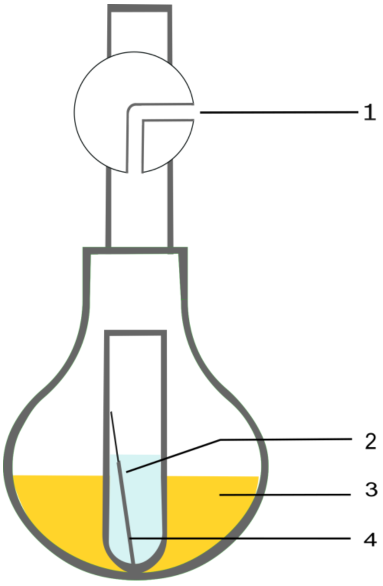
Tabela 1. Właściwości fizykochemiczne cieczy jonowych wykorzystanych w badaniach.

Akronim cieczy jonowej	Masa molowa $[g{*}mol^{-1}]$	Temperatura topnienia [°C]	Temperatura rozkładu [°C][1]	Gęstość $[g{*}cm^{-3}]$	Lepkość [cP]
IL-1	197.9	15.0	350.0	1.28	33.8
IL-2	453.4	<RT	396.0	1.49	153.0
IL-3	422.4	-6.0	360.0	1.40	95.0
IL-4	396.4	7.0	305.0	1.39	106.0
IL-5	426.4	-39.0	390.0	1.41	70.0

[1] – Dane otrzymane z pomiarów urządzeniem Netzsch TG 209 F3 Tarsus (badania zlecone). Warunki eksperymentalne: Argon, 25-800°C, zakres grzania 20°C min^{-1}.

Ostatnim etapem prowadzonych badań było unieruchomienie cieczy jonowej wewnątrz porów materiału krzemionkowego, pokrywającego włókno szklane. Proces prowadzono w szklanej kolbie okrągłodennej, przystosowanej do pracy w warunkach niskiego ciśnienia. Przygotowane włókna zanurzono w cieczy jonowej i umieszczono w kolbie wypełnionej olejem silikonowym, zapewniającej kontakt termiczny z komorą grzewczą, jak pokazano na Rys. 7.

Zastosowana procedura składa się z dwóch etapów: w pierwszym, za pomocą pompy próżniowej usunięto powietrze z porów powłoki; w drugim etapie, podwyższone ciśnienie wprowadziło ciecz jonową do porów powłoki. Pierwszy etap został zakończony na podstawie obserwacji, aż do momentu braku widocznych pęcherzyków gazu wydostających się z analizowanego włókna (ok. 120 minut). Podciśnienie uzyskano za pomocą pompy, dla której maksymalne podciśnienie było równe $2{*}10^{-2}$ mbar. Następnie, ciśnienie powoli było zwiększane, aż do ciśnienia atmosferycznego, w którym włókna były utrzymywane przez ok. 1 godzinę. Proces unieruchomienia cieczy jonowej do porów materiału silnie zależy od jej lepkości. Biorąc pod uwagę, że lepkość cieczy maleje wraz ze wzrostem temperatury, aby ułatwić penetrację cieczy jonowej do wnętrza porów, zastosowano możliwie najwyższą temperaturę. Niemniej jednak, docelowa temperatura była ograniczona temperaturą wrzenia oleju silikonowego pod próżnią, która wynosi ok. 1 godz. 150°C, dlatego w doświadczeniach za bezpieczną przyjęto temperaturę 120°C.



Rysunek 8. Schemat zestawu do unieruchomienia cieczy jonowej w porach materiału krzemionkowego: 1 – próżnia, 2 – ciecz jonowa, 3 – olej silikonowy, 4 – włókno SPME.

Główne, zmierzone i obliczone, parametry charakteryzujące otrzymane włókna do SPME przedstawiono w tabeli 2.

Tabela 2. Charakterystyka właściwości fizycznych wytworzonych włókien do SPME.

Włókno z cieczą jonową	Grubość powłoki [µm]	Długość powłoki [mm]	Objętość powłoki [µL]	Objętość unieruchomionej cieczy jonowej [µL]
1.	72.0	11.2	0.39	0.80
2.	90.0	11.5	0.47	0.55
3.	75.0	10.8	0.49	0.60
4.	68.0	10.5	0.44	0.40
5.	66.0	11.2	0.41	0.50

4.3. EWALUACJA I ZASTOSOWANIE DO EKSTRAKCJI - SZKŁO WODNE SODOWE JAKO PREKURSOR MATERIAŁU POROWATEGO

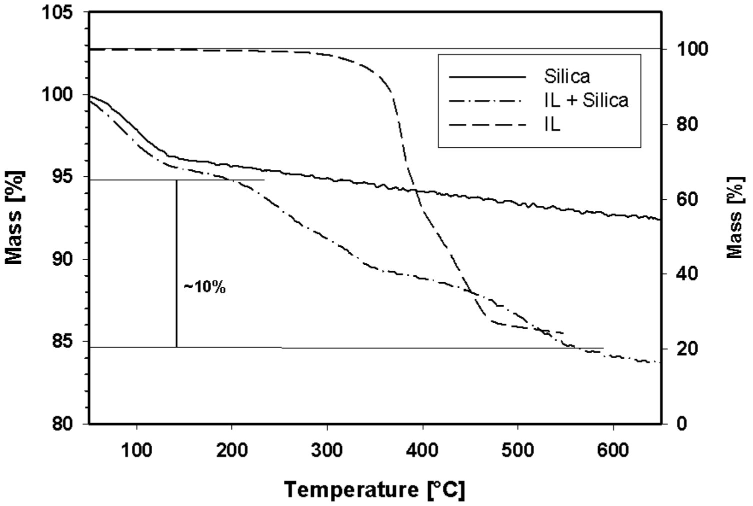
Otrzymane porowate włókno krzemionkowe z unieruchomioną cieczą jonową IL-1 zostało zainstalowane na komercyjnym urządzeniu SPME (Supelco, Bellefonte, PA). Ocena przydatności otrzymanego włókna została przeprowadzona za pomocą ekstrakcji lotnych związków organicznych ze standardowego roztworu wodnego techniką SPME z fazy nadpowierzchniowej (HS-SPME z IL-1). Do badań modelowych wybrano kilka lotnych związków organicznych o różnych wartościach współczynnika podziału oktanol-woda jako miary polarności (Log K_{ow}). Wybrano następujące LZO: toluen, etylbenzen, n-butylbenzen, m-xylen, 1,3,5-trimetylbenzen, 1,2,4-trimetylbenzen, p-izopropyltoluen, styren, bromobenzen, 1,2,4-trichlorobenzen, 1,2,3-trichlorobenzen, naftalen. Charakterystyka włókna użytego w badaniach została przedstawiona w Tabeli 3.

Tabela 3. Charakterystyka włókna użytego w badaniach.

Długość powłoki [mm]	Średnica włókna szklanego [µm]	Grubość powłoki [µm]	Średnica porów (średnia) [µm]	Odchylenie standardowe średnicy porów [µm]	Porowatość powłoki włókna [%]
11,0±0,1	150±2%[1]	65±5.7	0.33	0.061	57.3

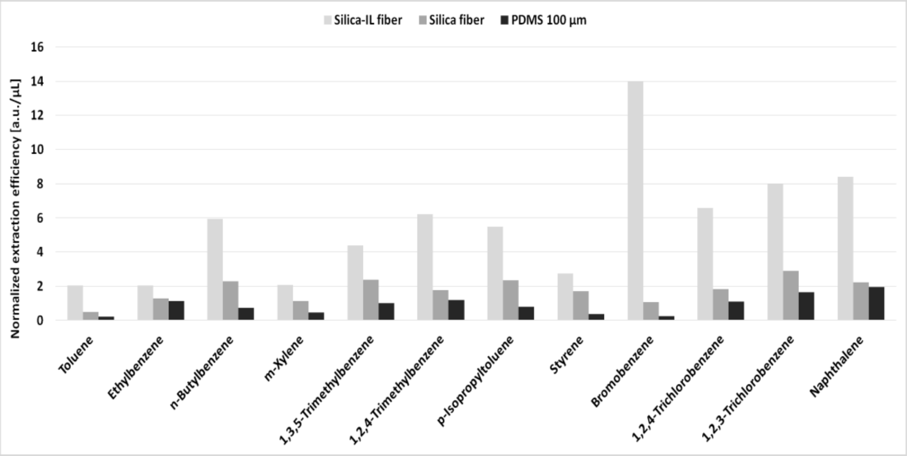
[1] – dane producenta (Supelco, Bellefonte, PA)

Objętość cieczy jonowej unieruchomionej w krzemionkowej sieci włókna obliczono na podstawie danych z analizy termograwimetrycznej (TGA). Odmierzone masy próbek włókien analizowano za pomocą TGA w atmosferze azotu, ogrzewając próbkę do 800°C (10°C/min). Termogramy uzyskane dla badanych włókien (włókno z i bez cieczy jonowej) oraz czystej cieczy jonowej zestawiono na Rysunku 8. Biorąc pod uwagę masę próbki użytej do pomiaru TGA (1,05 mg) i gęstość cieczy jonowej (1,294 $g_{*}cm^{-3}$ [47]), objętość cieczy jonowej unieruchomionej w porach materiału krzemionkowej wynosiła 0,8 µL.



Rysunek 9. Termogram czystej cieczy jonowej (linia przerywana), czystej krzemionki (linia stała) oraz materiału hybrydowego ciecz jonowa + krzemionka (linia kreska-kropka). Oś Y: lewa odnosi się do materiałów krzemionkowych i hybrydowych, prawa odnosi się do pomiarów czystej cieczy jonowej.

Procedurę ekstrakcji SPME przeprowadzono przy użyciu 12 ml standardowego roztworu wodnego zawierającego 20% (wagowo) Na_2SO_4. Mieszadło magnetyczne umieszczono w fiolce 15 mL, próbkę mieszano z prędkością 1800 obrotów na minutę, po czym fiolkę zamknięto nakrętką z septą, zaś roztwór termostatowano przez 20 minut w 45°C. Następnie, wstrzyknięto 10 µl roztworu podstawowego analitów i pozostawiono na 10 minut, w celu osiągnięcia równowagi termicznej. Włókno eksponowano w fazie nadpowierzchniowej próbki przez 30 min w 45°C. Na koniec, włókno wyciągnięto z fiolki i włożono do dozownika GC, w celu desorpcji termicznej w temperaturze 220°C, przez 10 minut. Rozdzielenie związków przeprowadzono przy użyciu chromatografu gazowego Agilent Technologies 7890A, wyposażonego w detektor płomieniowo-jonizacyjny (FID), na kolumnie kapilarnej SPB-5 (30 m x 0,32 mm ID; grubość warstwy filmu 0,25 µm), dozownik chromatografu działał w trybie splitless. Detektor utrzymywano w temperaturze 300°C. Zastosowano następujący program temperaturowy: ustawiono początkową temperaturę 40°C przez 10 minut, następnie temperatura wzrosła do 145°C (50°C/min), kolejno do 170°C (4°C/min), aż ostatecznie do 225°C (10°C/min), utrzymując daną temperaturę przez 2 minuty. Do badań użyto włókna z czystą porowatą krzemionką oraz włókna hybrydowego (ciecz jonowa unieruchomiona w materiale porowatym). Celem przeprowadzonych badań była weryfikacja przydatności otrzymanych włókien, nie zaś poszukiwanie optymalnych warunków ekstrakcji. Jako materiał odniesienia, do badań wykorzystano również włókno komercyjne PDMS 100µm. Porównanie zdolności ekstrakcyjnych wyprodukowanych włókien z komercyjnymi przeprowadzono wykorzystując powierzchnie pików chromatograficznych wyznaczonych dla badanych analitów. Biorąc pod uwagę różnice w średnicy i długości powłok, obszary normalizowano dzieląc je przez objętość fazy ekstrakcyjnej badanych włókien. Wyniki badań zostały przedstawione za pomocą Rysunku 9.



Rysunek 10. Znormalizowane powierzchnie pików chromatograficznych dla badanych włókien: porowata krzemionka, porowata krzemionka wypełniona cieczą jonową, PDMS. Stężenie analitów w próbkach wynosiło 83 µg$_*$ mL^{-1}.

Jak można zauważyć na podstawie Rysunku 9, suma powierzchni pików dla włókna krzemionkowego z unieruchomioną cieczą jonową w strukturze porów jest znacznie wyższa dla wszystkich analitów, niż odpowiednie wartości uzyskane przy użyciu włókna krzemionkowego bez cieczy jonowej. Powyższa obserwacja potwierdza znaczny potencjał absorpcyjny cieczy jonowej jako ekstrahenta oraz dominującą rolę IL w procesie ekstrakcji. Jako wiarygodny parametr oceny zdolności ekstrakcyjnych badanych sorbentów wybrano współczynnik wzbogacenia (EF). EF obliczono jako stosunek stężenia analitu w ekstrahencie do jego stężenia w badanej próbce. Wartości EF dla włókien krzemionkowych, krzemionkowych z cieczą jonową oraz PDMS podsumowano w Tabeli 4. Wyniki zamieszczone w tabeli wskazują, że włókna oparte na materiale krzemionkowym wykazywały lepsze powinowactwo do LZO w porównaniu z włóknem PDMS. Granice wykrywalności (LOD) metody HS-SPME-GC-FID dla 12 LZO dla włókna krzemionkowego z unieruchomioną cieczą jonową obliczono z wykorzystaniem wysokości najniższych wykrywalnych pików (zdefiniowany jako wartość stosunku sygnał/szum = 3). Otrzymane wartości LOD mieszczą się w zakresie od 0,46 μg L^{-1} dla naftalenu do 4,23 μg L^{-1} dla toluenu. Granice oznaczalności (LOQ) zostały obliczone w taki sam sposób jak LOD, tylko na podstawie stosunku sygnału do szumu wynoszącego 9, które znalazły się w zakresie 1,39-12,68 μg L^{-1}. Dodatkowo, powtarzalność pojedynczego włókna oraz pomiędzy różnymi egzemplarzami włókien została oceniona odpowiednio w drodze pięciu oraz trzech powtórzeń analiz. Wartość powtarzalności pojedynczego włókna określa powtarzalność metody i waha się od 3,2 do 12,6%. Z kolei średnia powtarzalność pomiędzy włóknami wynosi 16,1 % i nie przekracza wartości 34,1 %. Otrzymane wartości zostały zawarte w Tabeli 4. Co ciekawe, pojedyncze włókno może być użyte bez widocznego spadku wydajności przez około 50 cykli ekstrakcji/desorpcji. Po 50 cyklach wydajność ekstrakcji zaczyna systematycznie spadać poniżej ustalonej średniej wartości z poprzednich eksperymentów; tym samym założono, że 50 cykli ekstrakcji/desorpcji to dopuszczalny czas życia włókna.

Tabela 4. Charakterystyka analityczna opracowanej metody HS-SPME-GC-FID do oznaczenia LZO z wykorzystaniem badanego włókna krzemionkowego z cieczą jonową oraz współczynniki wzbogacenia włókna z czystą krzemionką, krzemionkowego z cieczą jonową oraz PDMS.

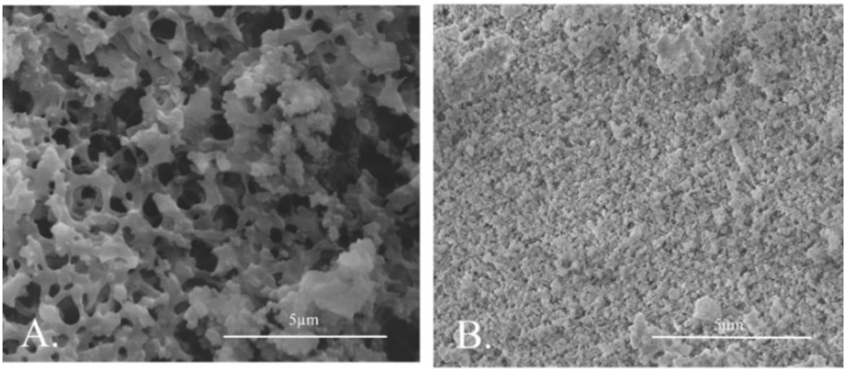
Związek	**Współczynnik wzbogacenia**			**Włókno krzemionkowe z cieczą jonową**			
	Włókno krzemionkowe	Włókno krzemionkowe z cieczą jonową	PDMS	LOD[1]	LOQ[1]	RSD[2]	RSD[3]
Toluen	1030	4360	390	4.23	12.68	10.9	34.1
Etylbenzen	3240	8700	3760	1.59	4.78	8.5	23.2
m-Xylen	2550	6430	1190	1.81	5.44	7.4	15.9
Styren	4750	8180	1150	1.55	4.66	7.9	15.9
Bromobenzen	4520	35190	840	1.62	4.86	5.4	14.9
1,3,5-Trimetylbenzen	5740	12800	2950	0.82	2.46	3.7	5.7
1,2,4-Trimetylbenzen	4390	16350	3760	0.77	2.32	6.6	19.2
p-Izopropyltoluen	5970	16150	2360	0.74	2.21	3.7	7.0
n-Butylbenzen	5860	18180	2270	0.65	1.96	12.6	29.4
1,2,4-Trichlorobenzen	8720	34420	6570	0.59	1.78	5.1	9.4
Naftalen	7800	32630	8870	0.46	1.39	3.6	10.9
1,2,3-Trichlorobenzen	13970	42100	10220	0.50	1.50	3.2	8.0

[1] - µg L^{-1}
[2] - RSD %, n=5, dla pojedynczego włókna
[3] - RSD %, n = 3, dla kilku włókien

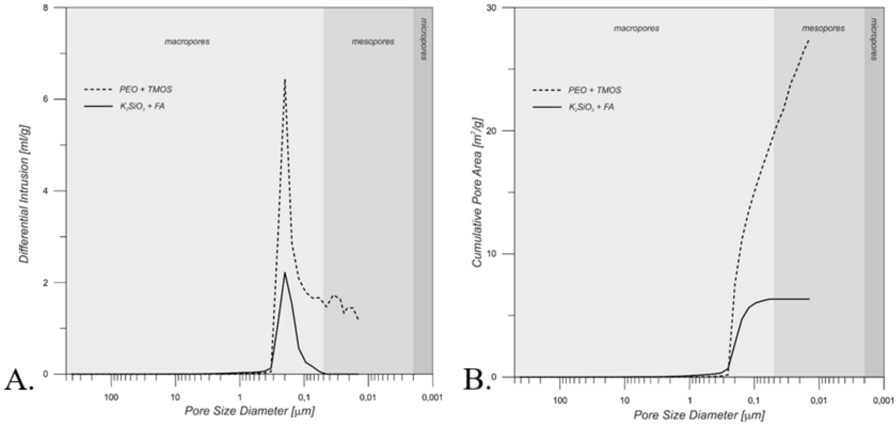
4.4. *TMOS, PEO, FA i K_2SiO_3 JAKO SUBSTRATY DO PRODUKCJI POWŁOKI KRZEMIONKOWEJ – OCENA MOŻLIWOŚCI EKSTRAKCYJNYCH WŁÓKIEN*

Badania nad możliwościami ekstrakcyjnymi opracowanych włókien zostały rozszerzone w kontekście użycia większej grupy mieszanin prekursor-substancja porotwórcza do produkcji powłok włókien SPME. Powłoki wytworzone z zastosowaniem szkła sodowego, jakkolwiek, wykazywały znacząca porowatość nie pozwalały na unieruchomienie adekwatnie dużych ilości cieczy jonowej. Z tego powodu w dalszych badaniach do wytwarzania powłok porowatych postanowiono zastosować inne układy prekursor-substancja porotwórcza.

Jak już wcześniej wspomniano (Rozdział 3.1.), w badaniach tych wykorzystano dwa układy materiałów prekursor-substancja porotwórcza: TMOS i PEO oraz K_2SiO_3 i FA. Oba z wybranych układów materiałów charakteryzowały się pożądaną, wysoką porowatością, na co wskazywały otrzymane wyniki analiz SEM (Rys. 11) oraz porozymetrii rtęciowej (Rys. 12), dlatego też, zdecydowano się na wykorzystanie obu układów materiałów jako włókien do SPME i zbadanie ich możliwości ekstrakcyjnych.



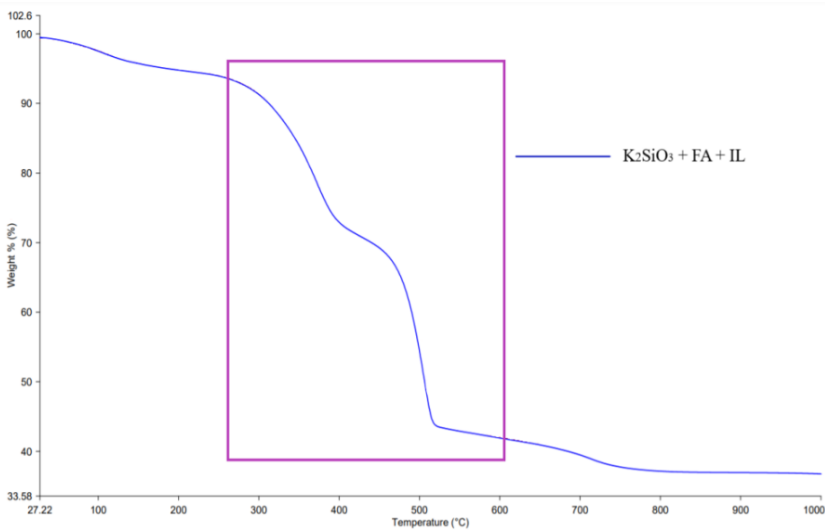
Rysunek 11. Zdjęcia SEM układów prekursor-substancja porotwórcza zastosowanych w przeprowadzonych badaniach: A. TMOS i PEO, B. K_2SiO_3 i FA.



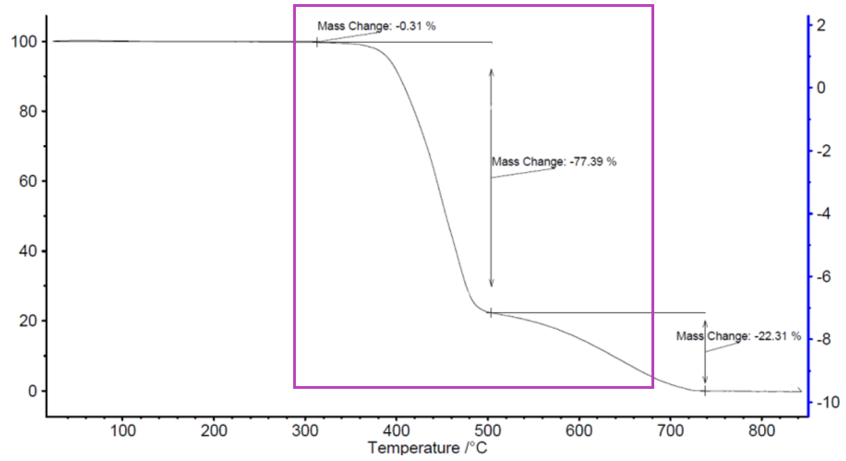
Rysunek 12. Wyniki analizy przeprowadzonej za pomocą porozymetrii rtęciowej dla analizowanych układów prekursor-substancja porotwórcza. A. Intruzja różnicowa a wielkość porów, B. Skumulowana powierzchnia porów. Klasyfikacja wielkości porów według IUPAC.

Rozważając otrzymane wyniki analiz SEM oraz porozymetrii rtęciowej, należy również wziąć pod uwagę praktyczne zastosowanie powłok jako włókien do SPME, które jest określane przez kilka właściwości. Do najistotniejszych należą te związane z oceną fizyczną, tj. regularność powłoki, jej grubość oraz wytrzymałość mechaniczna. Spodziewanym problemem podczas wykonywania prac badawczych było również zjawisko kurczenia się żelu krzemionkowego podczas czynności tzw. obróbkowych, np. starzenia, które odgrywałoby kluczową rolę w przygotowaniu powłoki. Oba z analizowanych układów prekursor-substancja porotwórcza zostały poddane wymienionym obserwacjom. Układ TMOS i PEO wykazywał zbyt dużą (niepożądaną) porowatość, dlatego do dalszych badań wybrano układ K_2SiO_3 i FA. Biorąc pod uwagę, że unieruchomienie cieczy jonowej w porach opiera się na działaniu sił kapilarnych, zbyt duża średnica porów wydaje się niepożądana. Jednocześnie stwierdzono, że obecność dużych porów w innych wariantach (Załącznik 4; Materiały dodatkowe; Tabela S1) przygotowanych roztworów krzemionki skutkowała zwiększoną kruchością materiału, co mogło skrócić żywotność włókien.

Kolejnym etapem przeprowadzonych badań było unieruchomienie cieczy jonowej w porach włókna SPME wykonanego z układu K_2SiO_3 i FA. W tym celu wykorzystano modelową ciecz jonową bis(trifluorometylosulfonylo)imid 1-benzylo-3-metyloimidazoliowy (IL-2). Weryfikacja unieruchomienia wybranej cieczy jonowej w porach materiału została przeprowadzona za pomocą analizy TGA, której wyniki zostały przedstawione na Rys. 13. Celem porównania, na Rys. 14 przedstawiono termogram dla czystej cieczy jonowej użytej w badaniach.



Rysunek 13. Termogram K_2SiO_3 i FA z unieruchomioną cieczą jonową.

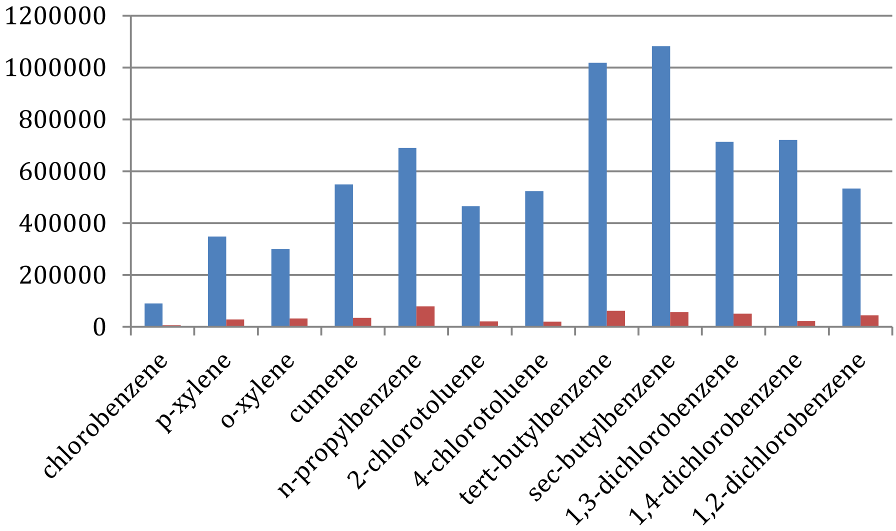


Rysunek 14. Termogram czystej cieczy jonowej IL-2.

Wyniki TGA dla obu materiałów (Rys. 13 i Rys. 14) wykazały spadek masy o 5% od 105°C. Możliwą przyczyną tego spadku jest zawartość wody, która została zaadsorbowana ze środowiska podczas przygotowania próbki. Między 220°C a 530°C można zaobserwować drugi, dwustopniowy spadek masy próbki zawierającej ciecz jonową. Nastąpiła również niewielka zmiana w szybkości ubytku masy około 420°C. Podobne zjawisko można zaobserwować w trakcie rozkładu czystej cieczy jonowej, co widać na Rysunku 13 (z granicą około 400°C). Na podstawie przeprowadzonej analizy TGA przyjęto więc ubytek masy (około 55%) w zakresie temperatur od 220°C do 530°C, jako konsekwencję rozkładu unieruchomionej cieczy jonowej.

Ostatnim etapem badań było sprawdzenie otrzymanego włókna w praktyce, poprzez zastosowanie go w rzeczywistej procedurze analitycznej. Sprawdzenie praktycznej przydatności włókna polegało na przeprowadzeniu cykli nagrzewania w dozowniku chromatografu gazowego w temperaturze 220°C, w atmosferze helu oraz wizualnej ocenie włókien co dziesięć cykli. Żywotność włókna określono na podstawie dwóch parametrów: oceny wizualnej, gdzie kryterium było powstawanie pęknięć i utrata części powłoki, drugim parametrem było monitorowanie ilości zatrzymywanych analitów – wydajność ekstrakcji włókna. Ta ostatnia metoda weryfikacji jest spowodowana tym, że nie jest możliwa wizualna ocena, czy nastąpiła utrata cieczy jonowej z porów materiału. Przyjęto kryterium, że utrata sprawności poniżej 80% wartości początkowej dyskwalifikuje dane włókno z dalszego użytkowania; ostatecznie zaobserwowano przeciętny czas życia włókien wynoszący 80 cykli sorpcji/desorpcji.

Ekstrakcję lotnych związków organicznych o różnej polarności przeprowadzono w trybie HS dla próbek wodnych. Celem tego etapu było zbadanie przydatności otrzymanych włókien, a nie kontrolowanie optymalnych warunków ekstrakcji. Eksperymenty przeprowadzono w warunkach typowych, wyznaczonych na podstawie dostępnej literatury [1]: czas desorpcji 10 min, temperatura desorpcji 220°C, czas ekstrakcji 30 min, temperatura ekstrakcji 45°C, stężenie soli 20% (Na_2SO_4), objętość próbki 12 ml, stężenie analitów w zakresie od 5 do 100 ppm.



Rysunek 15. Porównanie powierzchni pików chromatograficznych badanych analitów dla włókna krzemionkowego z unieruchomioną (kolor niebieski) oraz bez cieczy jonowej (kolor czerwony) w porach jego struktury.

Biorąc pod uwagę uzyskane wyniki, sumaryczna wartość powierzchni pików dla włókna krzemionkowego z cieczą jonową unieruchomioną w strukturze porów jest znacznie wyższa dla wszystkich analitów, niż wartości otrzymane odpowiednio z włókna krzemionkowego bez cieczy jonowej. Obserwacja ta potwierdza znaczny potencjał absorpcyjny cieczy jonowej jako medium ekstrakcyjnego, a także dominującą rolę cieczy jonowej w procesie ekstrakcji. Szczegółowy przebieg badań został opisany w Załączniku nr 4.

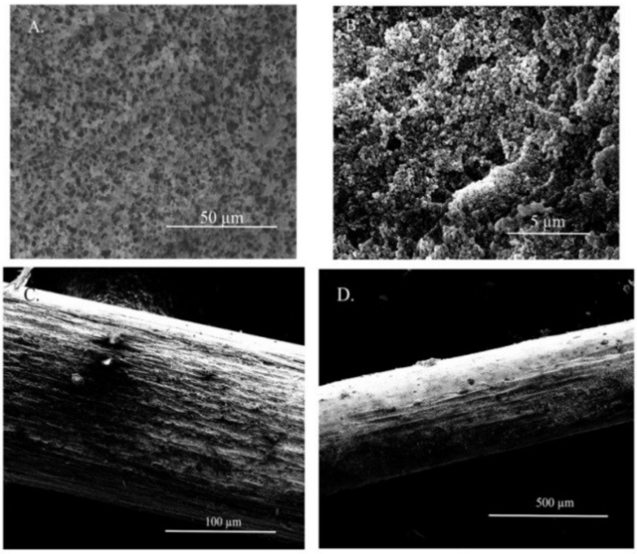
4.5. ZASTOSOWANIE WŁÓKIEN KRZEMIONKOWYCH DO OZNACZANIA INSEKTYCYDÓW ORGANOFOSFOROWYCH W PRÓBKACH WODNYCH I RZECZYWISTYCH

Badania nad możliwościami ekstrakcyjnymi opracowanego włókna z układu K_2SiO_3 i FA zostały rozszerzone w kontekście użycia większej grupy cieczy jonowych. Użyte w badaniach włókno SPME przygotowano w oparciu o wcześniej wykorzystywaną już procedurę, w skrócie obejmującą cztery etapy: wprowadzenie grup hydroksylowych na powierzchnię szkła, przygotowanie roztworu zolu, powlekanie zol-żelowe i obróbkę termiczną. W badaniach użyto czterech cieczy jonowych różniących się strukturą chemiczną kationów, unieruchomionych w porach materiału krzemionkowego. Są to wcześniej już wymienione w pracy ciecze jonowe IL-2, IL-3, IL-4 i IL-5 (Rozdział 3.2.). Z uwagi na pożądane właściwości ekstrakcyjne wykazane w pracy Załącznik 4, zdecydowano się na ponowne wykorzystanie IL-2 oraz porównanie jej z włóknami, w porach których unieruchomiono inne, wybrane ciecze jonowe. Włókna zastosowano do oznaczania insektycydów organofosforowych w próbkach wodnych i rzeczywistych.

Grubość i regularność otrzymanej powłoki włókna SPME oceniono wizualnie za pomocą mikroskopu optycznego (Rys. 16) oraz SEM (Rys. 17). Jak pokazano na rys. 16 (włókno przykładowe), można zauważyć, że otrzymana powłoka włókna charakteryzuje się regularnym kształtem i grubością oraz gładką powierzchnią bez widocznych pęknięć.

Rysunek 16. Włókno SPME ze wskazaną średnicą w powiększeniu 50-krotnym.

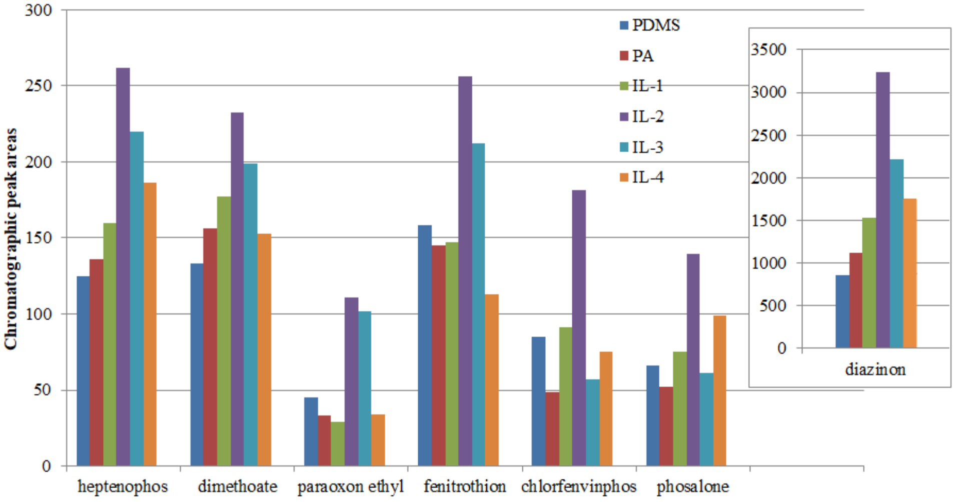
Wygląd, porowatość i regularność powłoki włókna zbadano również za pomocą SEM. Jak pokazano na Rys. 17, włókno charakteryzuje się widocznymi porami (o wyraźnej porowatości), o stosunkowo gładkiej powierzchni z minimalnymi nieregularnymi obszarami powłoki włókna.



Rysunek 17. Zdjęcia SEM opracowanego włókna.

W pracy wykorzystano cztery ciecze jonowe jako ekstrahenty. Wybrane ciecze jonowe mają ten sam anion bis(trifluorometylo-sulfonylo)imidowy, więc ich zdolność ekstrakcji zależy wyłącznie od kationu. Kationy różnią się pod względem polarności, zaczynając od mniej polarnego kationu butylotrietyloamoniowego (IL-4) i 1-butylo-1-metylopirolidyniowych (IL-1) zawierających w swojej strukturze tylko wiązania C-C sigma. Ciecz jonowa IL-3 zawiera dodatkowy pierścień aromatyczny i heteroatom tlenu, natomiast IL-2 zawiera dwa pierścienie aromatyczne. Ponadto, jako odniesienie zastosowano komercyjne włókna z powłokami PDMS (grubość 100 µm) i PA (grubość 85 µm). Porównanie zdolności ekstrakcyjnych wyprodukowanych włókien z komercyjnymi przeprowadzono wykorzystując powierzchnie pików chromatograficznych wyznaczonych dla badanych analitów (Rysunek 18).

Na podstawie wcześniejszych doświadczeń, parametry procedury analitycznej były następujące: 12 ml 20% wodnego wzorcowego roztworu Na_2SO_4 (w/w) w 15 ml szklanej fiolce; szybkość mieszania przy 1800 obr./min; termostatowanie w 55°C przez 20 minut. Następnie, 10 µl roztworu podstawowego wstrzyknięto do 12 ml roztworu wodnego i pozostawiono na 30 min do osiągnięcia równowagi termicznej. Włókno poddano działaniu ekstrakcji HS-SPME przez 35 min w 55°C. Na koniec, wyciągnięto go z fiolki i wprowadzono do dozownika GC w celu desorpcji termicznej w 220°C. Insektycydy desorbowano termicznie przez 10 min.

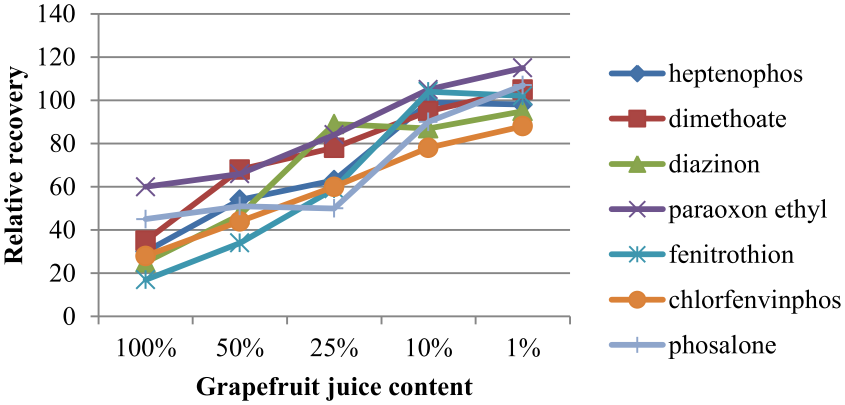


Rysunek 18. Porównanie zdolności ekstrakcji w stosunku do badanych insektycydów dla różnych ILs oraz referencyjnych włókien handlowymi PA i PDMS.

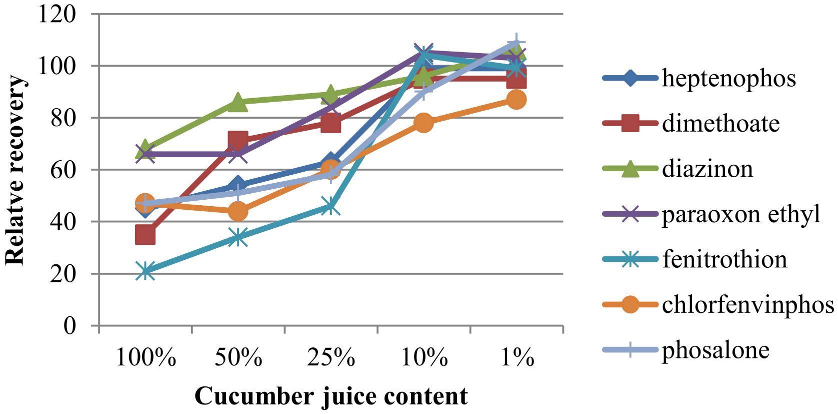
Biorąc pod uwagę różnice w objętości powłoki (fazy ekstrakcyjnej), obszary normalizowano dzieląc je przez objętość fazy ekstrakcji. Jak widać na Rys. 18, suma powierzchni pików dla włókna z unieruchomioną cieczą jonową IL-2 jest najwyższa dla wszystkich badanych insektycydów. W przypadku czterech z sześciu zastosowanych insektycydów, drugą najskuteczniejszą cieczą jonową była IL-3, zawierająca również polarny kation 1-(2-metoksyetylo)-3-metyloimidazoliowy. Jedynie w przypadku insektycydów zawierających pierścień benzylowy z podstawionym atomem chloru (chlorfenvinphos, phosalone), lepsze wydajności ekstrakcji uzyskano przy użyciu włókien niepolarnych, zarówno pod względem stosowanych cieczy jonowych, jak i powłok handlowych (PDMS). Z tego powodu, do dalszych badań wybrano włókno z unieruchomioną cieczą jonową IL-2.

Szczegółowe badania dotyczące optymalizacji warunków ekstrakcji oraz walidacji dla wybranego włókna zostały przedstawione w pracy Załączniku 5.

W końcowym etapie oceny przygotowane włókna wykorzystano do ekstrakcji próbek rzeczywistych. Ekstrakcję wybranych insektycydów fosforoorganicznych przeprowadzono z trybie HS-SPME dla próbek wody, ogórka i grejpfruta. Wpływ matrycy oceniono na podstawie zmiany wydajności ekstrakcji w zależności od stopnia rozcieńczenia soku. Zastosowano czysty sok oraz cztery jego rozcieńczenia, gdzie zawartość soku w próbce wynosiła 50, 25, 10 i 1% (obj.). Badania przeprowadzono w zoptymalizowanych warunkach. Wyznaczone zależności względnego odzysku dla badanych insektycydów w funkcji rozcieńczenia oryginalnych próbek soku przedstawiono na Rys. 19 (grejpfrut) i Rys. 20 (ogórek).



Rysunek 19. Wpływ rozcieńczenia próbek wodą w różnych stosunkach objętościowych rozcieńczenia (w/w) z wykorzystaniem cieczy jonowej IL-2 do ekstrakcji soku z grejpfruta.



Rysunek 20. Wpływ rozcieńczenia próbek wodą w różnych stosunkach objętościowych rozcieńczenia (w/w) z wykorzystaniem cieczy jonowej IL-2 do ekstrakcji soku z ogórka.

Jako punkt odniesienia wykorzystano wyniki ekstrakcji z próbek wody. Jak widać, w obu przypadkach efekt matrycy jest znaczący, gdzie obniżenie wydajności ekstrakcji wynosi odpowiednio od 20 do 60% i od 20 do 70% odpowiednio dla soku grejpfrutowego i z ogórka. W przypadku soku z ogórka o zawartości soku 10%, tylko dla chlorfenvinphosu względna wydajność była niższa niż 90%. Jednocześnie, osiągnięcie podobnego poziomu RR dla próbki grejpfruta wymagało 100-krotnego rozcieńczenia próbki. Można się jednak spodziewać, że wpływ matrycy dotyczy głównie podziału analitów między próbkę i fazę nadpowierzchniową. Założenie to mogą potwierdzić wyniki opublikowane przez innych autorów, w których stosowano różne rodzaje powłok ekstrakcyjnych [48-49].

Porównanie omawianej pracy zostało przedstawione z innymi przeprowadzonymi do tej pory badaniami naukowców w Załączniku 5.

5. WNIOSKI

Głównym celem badań opisanych w rozprawie było opracowanie nowych powłok porowatych na włóknie urządzenia do SPME umożliwiających unieruchomienie cieczy jonowych, w celu rozszerzenia zakresu stosowalności techniki SPME.

W trakcie studiów doktoranckich zrealizowano następujące zadania:

1. Opracowanie i udoskonalenie procedury pozyskiwania włókien SPME z krzemionkowych materiałów porowatych, z unieruchomieniem cieczy jonowych. Wykorzystano różne układy prekursor-substancja porotwórcza: Na_2SiO_3 i DMF, K_2SiO_3 i DMF, TMOS i PEO, K_2SiO_3 i FA. Najlepszym układem okazał się K_2SiO_3 i FA, wykazując pożądaną interakcję z cieczami jonowymi oraz najlepszą przyczepność do powierzchni włókna szklanego, w porównaniu z pozostałymi układami prekursor-substancja porotwórcza.

2. Rozwój zastosowania otrzymanych włókien dla większej grupy cieczy jonowych. W badaniach użyto łącznie pięć różnych cieczy jonowych, gdzie IL-1 była cieczą modelową, natomiast IL-2, IL-3, IL-4 i IL-5 zostały użyte w badaniach dotyczących możliwości ekstrakcyjnych wybranych cieczy jonowych. Włókna z unieruchomioną cieczą jonową IL-2 wykazały najwyższe zdolności ekstrakcyjne dla związków o różnej polarności.

3. Zastosowanie otrzymanych włókien do ekstrakcji różnych zanieczyszczenia z próbek wodnych. Włókna K_2SiO_3 i FA z unieruchomioną cieczą jonową IL-2 zostały poddanie ocenie w kontekście ekstrakcji lotnych związków organicznych. Za pomocą HS-SPME-GC-FID analizowano próbki wody. W badaniach porównywano zdolności ekstrakcyjne włókien z i bez cieczy jonowej na podstawie sumy powierzchni pików chromatograficznych analitów dla poszczególnych włókien. Badania wykazały znacznie wyższe wartości dla włókna z cieczą jonową, co potwierdza znaczny potencjał absorpcyjny cieczy jonowej jako medium ekstrakcyjnego, a także dominującą rolę mechanizmu absorpcji analitów przez ciecz jonową w procesie ekstrakcji.

4. Optymalizacja parametrów ekstrakcji procedury HS-SPME-GC-FID. Kluczowe parametry ekstrakcji, tj. czasy ekstrakcji i desorpcji, temperatury próbkowania i desorpcji, czas ustalania stanu równowagi oraz stężenie soli. Stężenie soli, pH, temperatura i czas ekstrakcji zostały szczegółowo zoptymalizowane dzięki zastosowaniu Centralnego Planu Kompozycyjnego *(ang. Central Composite Design - CCD)*.

5. Walidacja opracowanej metody i ocena efektu matrycy.

Parametry walidacyjne, takie jak LOD, LOQ, R^2, powtarzalność pojedynczego włókna i pomiędzy wytworzonymi włóknami, EE, zostały określone w celu oceny stosowalności proponowanej metody HS-SPME-GC-FID dla włókna z unieruchomioną IL-2. Wszystkie parametry wykazywały akceptowalne wartości. Wydajność włókna porównano również z włóknami komercyjnymi PDMS i PA. We wszystkich przypadkach znormalizowane wydajności ekstrakcji włókien krzemionkowych z unieruchomioną cieczą jonową są znacznie wyższe niż w przypadku włókien komercyjnych. Ostatecznie zaproponowane metody zostały zastosowane do analizy próbek rzeczywistych wody oraz próbek żywności (świeży sok z ogórka i grejpfruta). Zgodnie z uzyskanymi wartościami RRs, efekt matrycy nie był istotny dla próbek wody, natomiast miał znaczenie dla próbek soków.

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Załącznik 1

Application of ionic liquids in microextraction techniques: Current trends and future perspectives

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Application of ionic liquids in microextraction techniques: Current trends and future perspectives

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ABSTRACT

Ionic liquids (ILs) with their unique properties found so far numerous analytical applications. Among them ILs both in their liquid form and immobilized on the surface or within the pores of a solid support were successfully utilized in microextraction techniques. The scope of this review will cover a comprehensive summarizing of available literature data on selected properties of ILs playing a key role in analytical purposes, methods of their implementation in microextraction techniques as liquid or solid/stationary extraction media and finally, the most recent examples of application of ILs-based microextraction techniques in preconcentration of analytes from food, environmental and biological samples. The work will be concluded with directions for further investigation in this field.

1. Introduction

The philosophy of green analytical chemistry defines the principles allowing for pro-ecological activities in analytical laboratories [1]. Identification and quantification of compounds present in analytical samples at trace or ultra-trace levels usually requires a preliminary step of isolation of analytes. It is related to the performance of analytical instrumentation that in some cases is not enough sensitive for direct determination of analytes at such low levels of concentration. Several new technical and methodological solutions in this area have been proposed [2,3]. At the same time, we are obliged to minimize or even eliminate from the analytical methodologies harmful organic solvents and replace them with more friendly alternatives [4]. One of such groups of substances, named as solvents of the 21st century, are ionic liquids (ILs).

Following the ILs discovery over a century ago, they have become a significant field of studies in broad range of the chemical sciences. With a simple definition given by Paul Walden in 1914, ILs are commonly recognized as salts with a melting point below arbitrary temperature equal to 100°C. However, most often applied ILs are called room-temperature ionic liquids (RTILs) which are organic salts with melting points below room temperature [5]. Some of the most common cations and anions applied in analytical applications of ILs have been shown in Fig. 1. Looking at the constantly increasing number of papers concerned with RTILs application in chemical laboratories it may be said that there is a huge opportunity for them to be an alternative for conventional organic solvents in common sample preparation techniques. More than one thousand ILs are now known, and what is more, a lot of them are commercially available. Many important studies in physicochemical characterization of ionic liquids have been performed. Obtained knowledge allowed for conscious use of them in sample preparation techniques and other applications.

In the past two decades, the rapid increase in the number of papers reported the ILs use as sorption materials can be observed. This high popularity of ILs is related to their unique properties, especially, to these properties important from the “environmental” point of view i.e. negligible vapor pressure, high thermal stability, low flammability. However, it should be noted that the properties of ILs are highly influenced by their structure and presence of impurities. Furthermore, it is also necessary to understand how the physicochemical parameters of ILs are able to affect their affinity to selected groups of compounds. The relation between ILs properties and their structure will be shortly discussed in further section of this article.

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Abbreviations

$[\text{aliquat}+]_2\,[\text{MnCl}_4^{2-}]$	trioctylmethylammonium tetrachloromanganate(II)
$[\text{C}_2\text{C}_1\text{IM}][\text{Br}]$	1-ethyl-3-methylimidazolium bromide
$[\text{C}_2\text{C}_1\text{IM}][\text{Co(NCS)}_4]$	1-ethyl-3-methylimidazolium tetraisothiocyanatocobaltate(II)
$[\text{C}_2\text{C}_1\text{IM}][\text{BF}_4]$	1-ethyl-3-methylimidazolium tetrafluoroborate
$[\text{C}_2\text{C}_1\text{IM}][\text{Co(NCS)}_4]$	1-ethyl-3-methylimidazolium tetraisothiocyanatocobaltate(II)
$[\text{C}_3\text{C}_1\text{IM}][\text{FeCl}_4]$	1-propyl-3- methylimidazolium tetrachloroferrate(III)
$[\text{C}_4\text{C}_1\text{IM}][\text{Cl}]$	1-butyl-3-methylimidazolium chloride
$[\text{C}_4\text{C}_1\text{IM}][\text{PF}_6]$	1-butyl-3-methylimidazolium hexafluorophosphate
$[\text{C}_4\text{C}_1\text{IM}][\text{TFSI}]$	1-butyl-3-methylimidazolium bis(trifluorosulfonyl)imide
$[\text{C}_4\text{C}_1\text{IM}]\ [\text{FeCl4}]$	1-butyl-3-methylimidazolium tetrachloroferrate
$[\text{C}_4\text{C}_1\text{IM}][\text{Br}]$	1-butyl-3-methylimidazolium bromide
$[\text{C}_4\text{C}_1\text{IM}][\text{FeCl}^{4-}]$	1-butyl-3-methylimidazolium tetrachloroferrate(III)
$[\text{C}_4\text{C}_1\text{IM}]][\text{BF}_4]$	1-butyl-3-methylimidazolium tetrafluoroborate
$[\text{C}_6\text{C}_1\text{IM}][\text{PF}_6]$	1-hexyl-3- methylimidazolium hexafluorophosphate
$[\text{C}_6\text{C}_1\text{IM}][\text{Cl}]$	1-hexyl-3-methylimidazolium chloride
$[\text{C}_6\text{C}_1\text{IM}][\text{TFSI}]$	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
$[\text{C}_6\text{C}_1\text{IM}][\text{BF}_4]$	1-hexyl-3-methylimidazolium tetrafluoroborate
$[\text{C}_6\text{C}_1\text{IM}][\text{OAc}]$	1-hexyl-3-methylimidazolium acetate
$[\text{C}_6\text{C}_1\text{M}][\text{TFSI}]$	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
$[\text{C}_7\text{C}_1\text{IM}][\text{PF}_6]$	1-heptyl-3-methylimidazolium hexafluorophosphate
$[\text{C}_8\text{C}_1\text{IM}][\text{PF}_6]$	1-octyl-3-methylimidazolium hexafluorophosphate
$[\text{C}_8\text{C}_1\text{IM}][\text{Cl}]$	1-octyl-3-methylimidazolium chloride
$[\text{C}_{10}\text{C}_1\text{IM}][\text{Cl}]$	1-decyl-3-methylimidazolium chloride
$[\text{C}_{12}\text{C}_1\text{IM}][\text{Cl}]$	1-dodecyl-3-methylimidazolium chloride
$[\text{C}_{16}\text{C}_4\text{IM}][\text{Br}]$	1-hexadecyl-3-butylimidazolium bromide
$[\text{C}_{16}\text{C}_1\text{IM}][\text{2TFSI}]$	1-hexadecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
DDT	dichlorodiphenyltrichloroethane
$[\text{DVBIM}_2\text{C}_{12}][\text{2TFSI}]$	1,12-di(3-vinylbenzylbenzimidazolium) dodecane dibis[(trifluoromethyl)sulfonyl] imide
[VBHDIM][2TFSI]	1-4-vinylbenzyl-3-hexadecylimidazolium bis [(trifluoromethyl)sulfonyl]imide
DICAT	dicationic ionic liquid
D-μ-SPE	dispersive micro solid phase extraction
E-MIL-DLLME	enhanced magnetic ionic liquid – dispersive liquid-liquid microextraction
FT-IR	fourier transform infrared spectroscopy
GFAAS	graphite furnace atomic absorption spectrometry
GO	graphene oxide
HS-LPME	headspace liquid phase microextraction
IL-DLLME	ionic liquid dispersive liquid-liquid microextraction
IL-SDME	ionic liquid – single drop microextraction
IL-SPE	ionic liquid-solid phase extraction
IL-SPME	ionic liquid-solid phase microextraction
IL-TGO	ionic liquid-thiol-graphene oxide
IL-μE-DLLME	ionic liquid assisted micro-emulsion- dispersive liquid-liquid microextraction
IL-mE	ionic liquid based microextraction
MCNPs	magnetic cellulose nanoparticles
MIL	magnetic ionic liquid
MIL-IMSA	magnetic ionic liquids isothermal multiple-self-matching-initiated amplification
META-IL-DLLME	magnetic effervescent tablet-assisted ionic liquid dispersive liquid-liquid microextraction
ME-IL-VALLME	micellar extraction combined with ionic liquid based vortex-assisted liquid-liquid microextraction
MIL-M-SPE	magnetic ionic liquid coupled with micro-SPE
MNP@PAMAM@CD@IL	ionic liquid-coated and cyclodextrin-functionalized magnetic core dendrimer nanocomposites
MOF	metal-organic framework
$[\text{N}_{8,8,8,1}][\text{TS}]$	trioctylmethylammonium thiosalicylate
$[\text{N}^+_{1,8,8,8}][\text{FeCl}_4]$	trioctylmethylammonium tetrachloroferrate(III)
$[\text{P}_{4,4,4,8}][\text{Br}]$	tributyloctylphosphonium bromide
$[\text{P}_{4,4,4,12}][\text{Br}]$	tributyldodecylphosphonium bromide
$[\text{P}_{4,4,4,16}][\text{Br}]$	tributylhexadecylphosphonium bromide
$[\text{P}^+_{6,6,6,14}]_2\,[\text{MnCl}_4^{2-}]$	trihexyl(tetradecyl)phosphonium tetrachloromanganate(II)
$[\text{P}^+_{6,6,6,14}][\text{Dy(hfacac)}^{4-}]$	trihexyl(tetradecyl)phosphonium tetrakis(hexafluoroacetylaceto) dysprosate(III)
$[\text{P}_{6,6,6,14}{}^+][\text{Mn(hfacac)}^{3-}]$	trihexyl(tetradecyl)phosphonium tris(hexafluoroacetylaceto) manganate(II)
$[\text{P}^+_{6,6,6,14}][\text{Ni(II)(hfacac)}^{3-}]$	trihexyl(tetradecyl)phosphonium tris(hexafluoroacetylaceto) nickelate
PAHs	poly aromatic hydrocarbons
PANI	polyaniline
PCR	polymerized chain reaction
PCR-MIL-ITO	polymerized chain reaction magnetic ionic liquid indium titanium oxide
PEG-DIL	poly (ethyleneglycol) bis(methylimidazolium chloride)
PILs	polymeric ionic liquids
PMME	polymeric monolith microextraction
PPy	polypyrrol
PTh	polythiophene
QuEChERS	quick, easy, cheap, effective, rugged, and safe method
RDSE	rotating disk sorptive extraction
SCSE	stir cake sorptive extraction
SIL	solidification ionic liquids
SBSE	stir bar sorptive extraction
TGA-DTG	thermogravimetric analysis/derivative thermogravimetry
TSIL-DLLME	task specific ionic liquid – dispersive liquid-liquid microextraction
TSIL-USA-DLLME	task specific ionic liquid – ultrasound assisted – dispersive liquid-liquid microextraction
UASEME	ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME)
USA-DSL-MPM	ultrasound assisted - dispersive solid liquid - multiple phase microextraction
VA-D-μ-SPE	vortex assisted dispersive micro solid phase extraction
VA-IL-DLLME	vortex-assisted ionic liquid dispersive liquid-liquid microextraction
VWD	variable wavelength detector

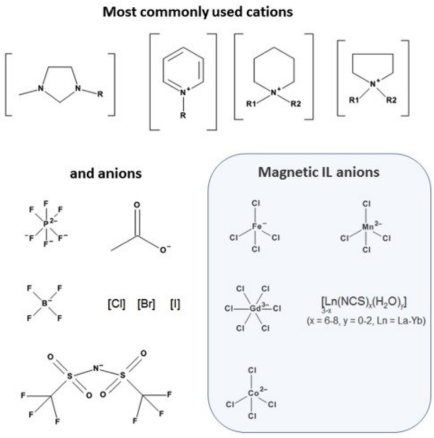

Fig. 1. Structure of typical ionic liquid cations and anions.

During last two decades, ILs have been applied as extraction phases in several important sample preparation techniques, i.e. solid-phase microextraction (SPME), dispersive liquid-liquid microextraction (DLLME), single-drop microextraction (SDME), stir bar sorptive extraction (SBSE), stir cake sorptive extraction (SCSE) [2,3]. Milestones in development IL-based microextraction techniques have been presented in Fig. 2.

At early stages of ILs application as sorption materials, several limitations have been observed, generally with unstable layer of IL on SPME fiber surface. After that, several solutions have been developed to support the use of ILs as extraction phases. One of these solutions are related to the fabrication of IL-based hybrid materials which based on immobilization of IL in/on porous solid material [6]. Other solution which supported significantly the use of ILs as sorbents is the development of polymeric ionic liquids (PILs). PILs are compounds that have polymerizable groups in cations or anions which allows for the formation of polymeric backbone in polymerization reaction. The major advantages of PILs are enhanced stability, flexibility, and durability in applications as practical materials [7]. In last years, a new subclass of ILs named magnetic ionic liquids (MILs) has been proposed. These magnetic solvents are produced by the incorporation of a paramagnetic component in either the cation or anion of the IL structure [8]. MILs have become a key subject in numerous recent ILs-based analytical applications [9]. In recent years, many reviews have been published presenting the current summary of the ILs application in the above mentioned microextraction techniques The vast majority of them thoroughly discuss the ILs properties as the function of anion, cation and type of substituent [10].

In this review, structures and properties of ILs relevant to extraction processes have been comprehensively discussed, which has been followed by the characterization of ILs-based liquid and solid/stationary extraction media implemented in microextraction and most recent literature examples of ILs applications in liquid phase and solid phase-based microextraction techniques. Advantages and shortcomings of several ILs-based novel sample preparation solutions have been summarized. Some trends have been also emphasized. It should be noted, that shortly after the first applications of ILs in microextraction techniques, a lot of review papers summarizing the state of the knowledge in this field were released [11–14]. There are also several review articles generally describing the usage of ILs in analytical chemistry field [15–17]. For this reason, this review is a comprehensive summarizing of most recent developments in the field of ILs-based microextraction, with paying special attention to such intensively exploited in the past few years topics as MILs and ILs-based hybrid materials.

2. Structures and properties of ionic liquids

One of the most important features of ionic liquids that distinguish them from other substances used as solvents in the extraction process is their negligible vapor pressure. It is widely believed that a defining characteristic of ionic liquids is that they exert no measurable vapor pressure, and hence cannot be distilled [18]. Nevertheless, it has been shown that under very low pressure at temperatures close to 200–300°C the vapor pressure of some ionic liquids can be measured [19]. Also vitally important ILs parameter is their high thermal stability. It has been proved that significant part of ILs tested so far decompose much above 200°C, and in some cases even over 450°C [20]. High thermal stability of ILs is strongly associated with their structure, particularly with the anion that forms the given ionic liquid [21]. Ionic liquids with less nucleophilic or coordinating anions usually exhibit the highest thermal stability (e.g., $[CF_3SO_3]$ and [TFSI]), while ILs with halide anions usually decompose in lower temperatures [22]. The influence of the cation on the thermal stability of ILs has also been studied [23]. Thus, for a ionic liquids with the same anion [TFSI], the thermal stability increased in the following series: $[C_4C_1Pyrr] > [C_4C_1IM] > [N_{4,1,1,1}] > [C_4C_1Py]$. The length of the alkyl substituent present in the cation structure does not have a significant influence on IL thermal stability [22].

One of the largest barriers to the application of ILs arises from their high viscosity. Typical ILs viscosity remain between 10 mPa s and 500 mPa s, which is a higher viscosity than in the case of classical organic solvents. For example, the viscosities of hexane, benzene and water at a room temperature are equal to 0.3, 0.6 and 0.9 mPa s, respectively. ILs cation is the most important structural factor affecting the viscosity, its nature and size is directly correlated with the viscosity of IL. The viscosity of ILs, which have the same kind of anion and the same length of the alkyl substituent chain in the cation increases in the following way for various cations: $[C_nC_1IM] < [Py] < [Pyrr]$. Moreover, the viscosity of ILs increases when the length of the alkyl chain attached to the cation increases [24]. In case of the anion, ionic liquids with large and non-symmetrical anions (like [TFSI] anion) exhibit lower viscosity than ILs with non-polar and symmetrical anions [25]. Another important factor affecting the ILs viscosity is temperature. As for the rest known organic solvents, viscosity of ILs decrease with increasing temperature and this dependence has an exponential shape [26].

Surface tension may be an important property in multiphase process. The surface tension values for ILs are somewhat higher than those for conventional solvents (e.g. hexane, 18 $mN\ m^{-1}$), although not so high as for water (73 $mN\ m^{-1}$) [27]. The type and size of the anion have the greatest influence on the surface tension of ILs. It decreases with increasing size of the anion: $[BF_4] > [PF_6] > [CF_3SO_3] > [TFSI]$ [28]. The influence of the cation can

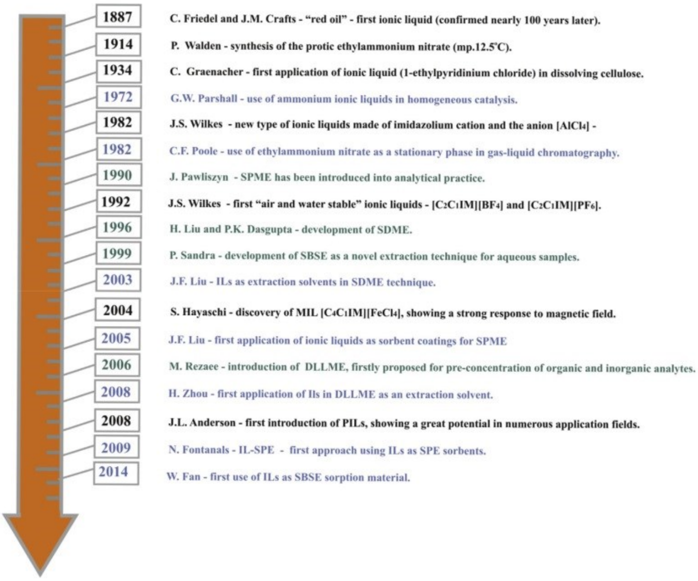

Fig. 2. Milestones of ionic liquids in sample preparation techniques – from the first synthesis toward microextraction application.

be observed but rather small. The lengthening of the alkyl substituent in the cation lowers the surface tension [28].

The solubility of ILs in water is a critical parameter for their use as separation media in extraction techniques. Therefore, it is important to explore the nature of ILs, in particular, the character of their interactions with various compounds. The strength of water-ion interactions for water-soluble ILs is mostly determined by the size of the ion. The solubility of ILs in water mostly depends on the anion [29], while the role of the cation is secondary. The hydrophobic nature of anions grows in the following order [Br] ~ [Cl] < [BF_4] < [PF_6] < [NTf_2] < [BETI] [30]. The role of the cation is dependent on the length of the alkyl substituent chain, as its increase results in an enhancement of the hydrophobic properties of the entire IL [31].

The term 'polarity' covers all the possible microscopic properties responsible for the interactions between ILs and analyte present in sample. Polarity of ILs decrease with anion size i.e. with the effective charge density. The presence of −OH or −OR groups in IL structure can vary the polarity of the corresponding IL over a wide range. Most widely used for IL empirical scale of polarity is the $E_{T(30)}$. This scale is based on wavelength maximum of the lowest energy π-π^* absorption band of the zwitteronic Reinchardt's dye. The $E_{T(30)}$ scale is often presented in normalized scale E_T^N, obtained by assigning water the value of 1.0 and tetramethylsilane zero [32]. For the 1-alkyl-3-methylimidazolium ionic liquids the E_T^N values are similar to that for ethanol. Elongation of the alkyl chain in cation reduce the IL polarity. Alteration of the anion in [C_4C_1IM]-based ionic liquids has very low effect on the E_T^N values [35]. A graphical representation of the E_T^N solvent polarity scale is given in Fig. 3.

3. Ionic liquids-based extraction media for microextraction techniques

The fact that ILs are "designer solvents", possible to be designed from vast number of anions, cations and alkyl substituents in cations in a way that defined compounds have a strong affinity towards them, makes them an indispensable group of extraction media for sample preparation techniques. For this purpose, they may be applied both as liquid extractants, where ILs native properties are kept, and ILs-based solid/stationary phases, which may be classified as new sorption materials benefiting from not only some of the native properties of ILs but also demonstrating other attractive features at the same time. There are also several issues limiting the designing of IL-based microexraction systems. All these aspects will be discussed in the following subsections. Fig. 4 presents the number of papers describing application of ILs as sorption materials in selected microextraction techniques in last five years.

3.1. *ILs as liquid extractants in liquid-phase microextraction techniques*

Extraction by a liquid, usually by an organic solvent, is one of the first solutions which comes to analytical chemist's mind when the isolation of analytes from a solid or liquid matrix is needed. Although still present in analytical practice, such well-known and rather old techniques as Soxhlet extraction or liquid-liquid extraction in separation funnels, require the use of high amounts of toxic and flammable solvents and, in addition, are very time-consuming. The recommendations covered in green chemistry

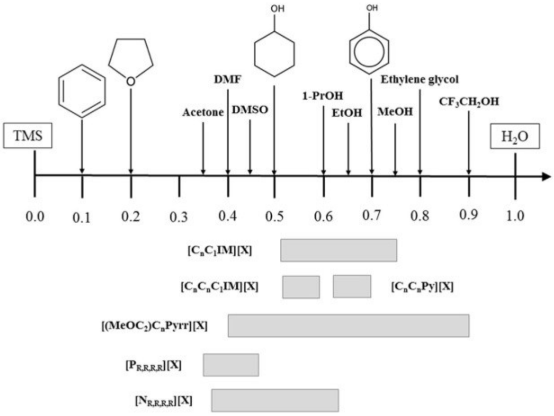

Fig. 3. Normalized solvent polarity scale with ordering to selected organic solvents and ionic liquids [35].

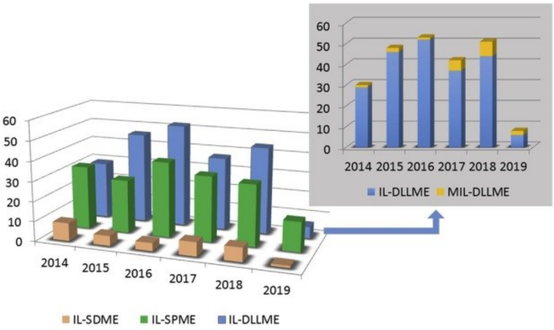

Fig. 4. Number of scientific papers with ionic liquids application in microextraction techniques in last five years (Web of Science, March 2019).

and later in green analytical chemistry principles released to the wider audience in fostered the replacement of above mentioned techniques by more user-safe and environmentally benign solutions. At first, solvent extractions were started to be assisted by e.g. microwaves, ultrasounds and elevated pressure which allowed for reducing solvent consumption, waste generation and time needed for complete analyte recovery. Further "green" modifications in the process of analytical extraction by a liquid were based on miniaturization and limiting the volume of solvents to 100 μl or less, which resulted in the development of currently such widely applied sample preparation techniques as single-drop microextraction (SDME) and dispersive liquid-liquid microextraction (DLLME) and their numerous, more specific modifications (e.g. drop-to-drop-SDME, droplet-membrane-droplet-LPME, electro membrane extraction, DLLME-solidification of a floating drop, etc.). Different modes of these techniques as well as other more specific solutions in liquid-phase microextraction have been comprehensively reviewed in several review papers [3,33,34].

The potential of ILs as environmentally friendly extraction solvents has been reported already in 1998 [35] after the investigation on the partitioning of substituted benzene derivatives between water and butylmethylimidazolium hexafluorophosphate. Taking into consideration their unique properties such as ability to solvate organic, organometallic and inorganic compounds, immiscibility in water as well as negligible vapor pressure, ILs appeared to the wider audience as an alternative to organic solvents in designing liquid-liquid extraction (LLE) systems. No wonder ILs started to replace conventional toxic solvents also in miniaturized liquid-phase systems, providing in this way solutions which are effective, selective and "clean" in the same time. Even though high viscosity of ILs and their higher cost in comparison to traditional organic solvents are usually considered as serious limitations in the context of their applicability in LLE, carrying out analytical extractions at microscale level allows for marginalizing them and taking the full advantage of ILs solvation power. Contrary to molecular solvents, ILs' differ from each other with solvation properties, which are highly dependent on their chemical structure and intermolecular interactions. These specific properties are the result of a spatial arrangement of IL in the bulk. This leads to the formation of domains characterized by different polarity, where during dissolution process compounds gather in the areas where they can form polar (e.g. hydrogen bonding) or nonpolar (e.g. π-π) interactions [36]. Because of a strong relation between cation and anion properties and IL's solvation power, a specifically designed IL is able to dissolve a defined group of substances such as polar/nonpolar compounds, metals, biopolymers etc. [37,38]. For example, by introduction into IL's structure such specific functional groups as thiourea and thioether ones, dissolution efficiency of cadmium and mercury is increased [39]. Solvation power of ILs is a fundamental aspect of their successful applicability as liquid extractants. Next to it, there are other unique features which make ILs suitable for a defined LPME technique. Some of the features however pose also several limitations in the context of ILs application in these techniques. Apart from being discussed below, the relevant information on both aspects have been also summarized in Table 1.

IL-based SDME benefits from negligible vapor pressure of ILs, which allows for the formation of stable drops staying in liquidous form during extraction in HS mode. Drop formation is also supported by somewhat higher surface tension of ILs (33–57 mN m^{-1}) [10] in comparison to conventional solvents (e.g. 18 mN m^{-1} for hexane) [27]. These factors in turn improve analytical performance (enrichment factor, precision) of the analytical methodology. High thermal stability of ILs provides the possibility of analytes thermal desorption without the risk of decomposition, thus IL may be recovered for further extractions and, in addition, the system is not contaminated by thermal decomposition products. Water-insoluble ILs may be successfully applied in isolating the analytes from aqueous samples by DI-SDME (direct injection SDME) [12] (see Table 2).

DLLME is another LPME technique which took the advantage of utilizing ILs as extraction solvents. Although considered as rather environmentally benign solution, DLLME is often depreciated because chlorinated solvents are most often selected as extraction solvents – they are heavier than water (after centrifugation the extraction phase is sedimented at the bottom of the vial and convenient to be collected and further analyzed), readily soluble in it and provide high extraction efficiencies. There were some attempts to replace these toxic solvents with long-chain alcohols or hydrocarbons, but employing in DLLME technique extractants lighter than water forced the implementation of specific devices and procedures, so such approach did not find wider applicability [40]. Because the density of most ILs exceeds water density, they appeared to the wider audience as a reasonable alternative to toxic chlorinated solvents for DLLME technique. This difference in density also provides an effective phase separation after centrifugation. Apart from hydrophobic ILs, which are an obvious choice for DLLME, several research groups also reported the application of hydrophilic ILs solely, without the need of using the water-soluble dispersing solvent. By manipulating the temperature [41] or counterion type [42], the authors initially induced complete dispersion of hydrophilic IL in the aqueous solution (providing large surface contact between IL and the sample) which was then followed by obtaining a turbid solution, subsequently centrifuged. In temperature controlled IL-based DLLME by heating and cooling the IL-sample mixture, the solubility of IL in water was tuned. In the second case, the addition of ion-exchange reagent promoted the *in-situ* formation of hydrophobic IL. In the end, enriched IL may be easily separated from the aqueous sample and collected for further analysis. These and other modes of operation in IL-based DLLME has been nicely reviewed in 2013 [43]. In most of the latest modifications in IL-based DLLME, the authors suggest novel solutions for

Table 1
Advantages and limitations in the application of ILs in the extraction process related to their properties.

Feature of IL-based liquid extraction phase	Advantage	Limitation
Negligible vapor pressure	- micro-amounts of extraction phase does not evaporate during extractions under elevated temperatures, extended duration time or in assistance of US/microwaves, which improves extraction efficiency and analytical precision; - temperature-controlled DLLME without the need of applying a dispersing solvent may be proceeded	- lack of a direct compatibility with GC system
High viscosity	- reduced risk of the loss of extraction phase located in HF pores and lumen during vigorous stirring of the sample	- difficulties in precise drop manipulation with a mycrosyringe (in SDME); - reduced diffusion and mass transfer rates; - the risk of incomplete introduction of enriched IL into detection/quantification system
High thermal stability	- reduced risk of thermal decomposition during thermal desorption of extracted analytes; - reduced risk of detection/quantification system contamination; - no ghost signals complicating evaluation of the results	- high temperature needed during the pyrolysis step in atomic detection systems may lead to analyte losses (analyte stabilizers needed)
Tunable solubility in water	- tuning the solubility in water during DLLME allows for obtaining complete dispersion and increased mass transfer to IL phase which is subsequently reversed in order to separate the phases and collect the enriched IL for further analysis; - water-immiscible ILs may be applied in DI-SDME and HF-LPME - hydrophilic MILs may be applied in DLLME-based extractions of hydrophobic matrices	–
Higher density than water	- possibility to replace toxic chlorinated solvents in DLLME; - the difference in density between IL and aqueous sample allows for effective phase separation	–

Table 2
Applications of ionic liquids in microextraction techniques.

Analytes	Ionic liquid	Sample preparation technique	Sample	Analytical technique	LOD (μg L^{-1})	LOQ (μg L^{-1})	RSD (%)	Linear range (μg L^{-1})	Recovery (%)	Ref.
SDME										
9 organophospho-rus pesticides	[C$_4$C$_1$IM][Cl], [C$_6$C$_1$IM][Cl], [C$_8$C$_1$IM][Cl], [C$_{10}$C$_1$IM][Cl], [C$_{12}$C$_1$IM][Cl]	in situ-IL-DLLME	environmental water: rivers	GC-MS	0.017 −0.054	0.033 −0.064	4.10−9.70	0.0001 to 0.002	85−118	[48]
5 organochlorine pesticides	[C$_4$C$_1$IM][PF$_6$],	HS-LPME	soil	GC-ECD	0.0001 −0.0005-	N.A.	8.86−15.30	0.005−0.25	N.A.	[49]
PCBs and acrylamide	[OMIM][Br]	in-situ DLLME	milk and coffee	HS-GC-ECD-MS	0.005 −0.025	N.A	3.9−13.8	0.025−5	N.A.	[50]
Hg	GO-PIL sorbent	CV-ILHAS-SDME	sea water, fish tissues, hair and wine	ETAAS	0.01	N.A	4.0−6.0	N.A.	96−104	[51]
ascorbic acid	[C$_4$C$_1$IM$^+$][FeCl$_4$]	MIL-SDME	vitamin C (effervescent tablets); orange juice	voltammetry	0.043	N.A.	10.0−25.0	0.015−0.04	101−104	[71]
8 volatile free fatty acids	[Aliquat]$_2$ [MnCl$_4$], [P$_{6,6,6,14}$]$_2$ [MnCl$_4$], [P$_{6,6,6,14}$] [Dy (hfacac)] [P$_{6,6,6,14}$] [Mn (hfacac)]	HS-SDME	low fat milk and organic fat reduced milk	GC-MS	14.5−70.3	48.4−721	2.5−13.0	0.1−13	79.5−111	[72]
8 chlorobenzenes	[C$_2$C$_1$IM]$_2$ [Co(NCS)$_4$]	HS-SDME	tap pond, water and wastewater	TD-GC-MS	0.004 −0.008	0.0013 −0.0025	N.A.	0.05−5	82.00 −114.00	[73]
12 aromatic compounds	[P$_{6,6,6,14}$]$_2$ [MnCl$_4$]	HS-SDME and DLLME	lake water	HPLC-UV	0.04−1.0	N.A	4.6−24.7	0.2−600	70.2−109.6	[74]
DNA	[P$_{6,6,6,14}$] [Ni(hfacac)]	MIL-IMSA	DNA samples	N.A.	N.A	N.A	N.A	N.A	N.A	[76]
DNA	PIL-based sorbent	MIL-SDME-	complex biological samples	N.A.	N.A	N.A	N.A	1.8−4.6	N.A	[77]
3 fungicides	[HMIM][PF$_6$]	ZnO−NF-SDME	Lake, river, effluent and influent waters	HPLC-VWD	0.00013 −0.00019	0.00044 −0.00063	4.7−7.0	0.5−100	74.9−96.1	[78]
DLLME										
PCBs and acrylamide	[OMIM][Br]	in-situ DLLME	milk and coffee	HS-GC-ECD-MS	0.005 −0.025	N.A	3.9−13.8	0.025−5	N.A.	[50]
4 hydroxylated PAHs	[C$_{10}$Gu][Cl]	salt-induced DLLME	urine	HPLC-FLD	0.002 −0.0005	lower than 0.005	2.4−6.6	N.A.	95.1−110	[83]
4 pyrethroid pesticides	[P$_{4,4,4,8}$][Br] [P$_{4,4,4,12}$][Br] [P$_{4,4,4,16}$][Br]	in-situ MR-IL-DLLME	tap water, pond water, river water, lake water	HPLC-MS/MS	0.16−2.10	N.A.	2.54−4.55 (intra-day) 4.49 −6.84 (inter-day)	1−100	80.20 −117.31	[84]
4 acaricides	[OMIM][TFSI]	IL-TiO$_2$-EA-DLLME	honey and tea	HPLC-DAD	0.04−0.18	0.13−0.60	2.32−5.71	0.5−500	70.70 −84.58	[85]
28 benzodiazepines and benzodiazepine-like hypnotics	[C$_4$C$_1$IM][PF$_6$] [C$_6$C$_1$IM][PF$_6$] [C$_2$C$_1$IM][PF$_6$]	IL-DLLME	blood	HPLC−MS/MS	0.000003 −0.00474	0.002−0.05	2.92−10.40	0.002−0.25	24.7−127.2	[86]
DNA sequences	[ABzIM][Br], [AMIM][Br], [ABIM][Br], [AOIM][Br]	MIL-ITO	complex biological samples	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	[87]
8 lipophilic organic UV filters	[P$_{66614}$] [Co(III)(hfacac)], [P$_{66614}$] [Ny(III)(hfacac)],	SBDLME	river, sea and swimming pool water	TD-GC-MS	9.9−26.7	32.5−88.2	1.4−14.7	0.05−0.25	87−117	[93]
SPME										
aromatic volatile compounds	[C$_4$C$_1$IM][TFSI]	HS-SPME	mineral, tap and ground water	GC-BID	0.03−1.27	0.11−4.24	5.6−12.0	75	88.7−113.9	[94]
7 chlorinated organic pollutants	[C$_4$C$_1$Py][TFSI], [C$_4$C$_1$Pyrr][TFSI], [C4C1Pip][TFSI]	HS-SPME	mineral, tap and ground water	GC-BID	0.011 −0.151	0.037 −0.503	6.7−9.6	100	95−106	[95]
6 organophosphorus pesticides	[C$_{16}$C$_1$IM][TFSI]	HS-SPME	river and tap water, municipal sewage	GC-FID	0.04−0.95	N.A.	9−13	0.5−50	64.8−125.4	[96]
4 PAHs	IRMOF-3@ILs/PDMS	HS-SPME	rain water	GC-MS	0.012 −0.154	N.A.	1.5−9.6	0.05−20	N.A.	[97]
8 organochlorine pesticides	[(SiC$_2$O$_x$)C$_3$C$_3$IM][PF$_6$]	HS-SPME	juice and milk	GC-ECD	0.11−0.29	0.35−0.93	4.4−10.1	1−500	76.1−121.3	[98]
9 UV filters	[VC$_1$C$_{10}$][SS], [(VBC$_1$)$_2$C$_{12}$][2SS]	DI-SPME	pool, tap and lake water	HPLC-UV	0.1−5	N.A.	1.8−11.6	0.2−200	66.6−118.5	[99]
5 volatile endocrine-disruptor pesticides	[C$_8$MC$_1$IM][Br], [C$_{12}$C$_1$IM][Br], [C$_{18}$C$_1$IM][Br]	HS-SPME	green and black tea drinks	GC-ECD	0.000002 −0.000667	0.000025 −0.002224	7.1−17.8	0.00001 −0.0003	88.7−101.7	[100]

(continued on next page)

Table 2 (*continued*)

Analytes	Ionic liquid	Sample preparation technique	Sample	Analytical technique	LOD (μg L^{-1})	LOQ (μg L^{-1})	RSD (%)	Linear range (μg L^{-1})	Recovery (%)	Ref.
6 alcohols	[HOEMIM]BF$_4$], [HOEMIM][TFSI], [C$_4$C$_1$IM][BF$_4$]	HS-SPME	soft drinks	GC-FID	0.0022 −0.0283	N.A.	3.8−5.6	0.005−250	85.6−114	[102]
11 aromatic compounds	polypyrrole-[C$_6$C$_1$IM]	HS-SPME	water	TGA-DTG	N.A.	N.A.	N.A.	N.A.	N.A.	[103]
6 phenolic compounds	PILs	DI-SPME	groundwater	HPLC-UV	0.2−0.5	N.A.	04.06.2013	1−400	75.5−113	[104]
4 carbamate pesticides	[VHIM][TFSI], [VEIM][TFSI], [VEIM][Br]	DI-SPME	apple and lettuce	GC-FID	0.0152 −0.0272	N.A.	4.7−8.2	0.05−250	87.5−106.5	[66]
10 PAHs	[VOIM][Br]	in-tube SPME	soil and coal ash aqueous samples	HPLC-UV	0.010 −0.020	0.35−3.18	0.2−1.8	0.03−20	85.1−118.9	[106]
4 phtalates	[C$_{12}$V$_3$IM][Br]	in-tube SPME	water	HPLC-UV	0.01−0.05	N.A.	0.5−4.6	0.03−12	86.4−119.5	[107]
anandamide (AEA) and 2-arachidonoyl glycerol (2 AG)	[V$_1$C$_{16}$IM][Br] [(VIM)$_2$C$_{10}$]$_2$ [Br]	in-tube SPME	plasma	UHPLC-MS/MS	N.A.	0.0001 −0.00005	(−)19.6−13.2	0.0001−0.1	N.A.	[108]
DDT and its main metabolites	[C$_{16}$C$_1$IM][TFSI]	HF-SPME	river, tap and sewage water	UHPLC−UV	0.33−0.38	1.0−1.25	1−16.2	0.5−50	64−112	[109]
DNA	PIL-based SPME	SPME	complex biological samples	HPLC-UV	N.A.	N.A.	2.7	N.A.	N.A.	[110]
DNA	[(C8)3BnN] [FeCl3] [(C16BnIM)$_2$C$_{12}$] [TFSI], [FeCl$_3$], [P$_{6,6,6,14}$] [FeCl$_4$]	SPME	aqueous solution of mRNA samples	HPLC-UV	N.A.	N.A.	1.6−8.7	N.A.	N.A.	[111]
DNA	PIL-IMSA	SPME	artificial sputum samples	IMSA	N.A.	N.A.	3.1	N.A.	N.A.	[112]
Dispersive sorption-based techniques										
lorazepam and nitrazepam	Fe$_3$O$_4$ nanocomposites modified by polyaniline, polypyrrole, and aniline-pyrrole copolymer	D-μ-SPE	human urine samples	HPLC-UV	0.2−2.0	N.A.	4.1−7.8	1−2000	84−99	[113]
10 steroids and beta-blockers	[C$_4$C$_3$IM][NH$_2$]	micro-SPE with GO-IL	effluent from a municipal wastewater treatment plant, natural water samples from two rivers and a lake	HPLC-DAD	0.007 −0.023	0.02−0.07	3.1−8.5	N.A.	87−98	[114]
PAHs	ionic liquid-modified metal −organic frameworks (IL-MIL-100(Fe)),	VA-D-μ-SPE	water, vegetable, and fruit juice samples	GC-FID	0.002−0.2	N.A.	3.0−4.9	0.00002 −0.2	N.A.	[116]
Pb(II), Cd(II), Ni(II), Cu(II) and Cr(III)	ionic liquid modified magnetic graphene oxide (DIL-MGO)	UA- DIL-MμSPE	medicine capsules	FT-IR	0.2−1.8	0.66−6.1	1.80−4.04	1.1−150	95.4−102.4	[117]
3 pyrethroids	MNP@PAMAM-with beta -CD-O-T	d-M-SPE	water, vegetable, and fruit juice samples	HPLC-DAD	0.36−1.3	1.2−4.3	1.9−5.4	3.5−500	95.2−97.5	[118]
3 acaricides	C$_{16}$C$_1$Br-coated attapulgite/ polyaniline-polypyrrole/Fe$_3$O$_4$ (ATP/PANI-PPY/ Fe$_3$O$_4$) nanocomposites	MMHDSPE	fruit juice	FT-IR, XRD	0.16−0.57	N.A.	0.19−8.36	2.5−500	88.67 −95.10	[120]
pharmaceuticals and personal care products (PPCPs)	PEG-modified silicone compared with PDMS Twister	SBSE	wastewater and effluents	LC-MS/MS	0.23−0.31	N.A.	6.5−12.1	1−500	77.0−114.0	[121]
3 NSAIDs	[BMIM][PF$_6$], [AIM] [BF$_4$], [AMIM][BF$_4$], [AEMIM][BF$_4$]	SBSE	environmental water, urine, and milk samples	HPLC-UV	0.23−0.31	N.A.	7.5−9.5	1−500	93.9−110.8	[122]
6 extrogens	synthesized AVED	SCSE	lake, reservoir and river water	HPLC-DAD	0.024 −0.057	0.08−0.19	1.95−5.43	0.1−200	72.1−108	[123]
3 organic acid preservatives	AVDVB (1-ally-3-vinylimidazolium	SCSE	orange juices and tea drinks	HPLC-DAD	0.012−0.23	0.039−0.42	below 10%	N.A.	71.9−116	[124]

Table 2 (*continued*)

Analytes	Ionic liquid	Sample preparation technique	Sample	Analytical technique	LOD ($\mu g\ L^{-1}$)	LOQ ($\mu g\ L^{-1}$)	RSD (%)	Linear range ($\mu g\ L^{-1}$)	Recovery (%)	Ref.
	chloride (AV) and divinylbenzene (DVB))									
10 PCBs	[C_6C_1IM][Br]	RDSE	water	XRD	0.003 −0.043	N.A.	2−24	2.1−24.8	35.8−55.5	[125]
synthetic phenolic antioxidants	melamine-based covalent organic polymer (MCOP) and ionic liquid (IL); [BrC_6V_1][Br]	PMME	cosmetics samples including essence and toner	HPLC-UV	0.0001 −0.0003	0.0003 −0.0008	below 10%	N.A.	71.6−109.2	[126]

N.A. - not available.

fine dispersion formation and effective enriched IL separation before final analysis in a simplified way, based mainly on the application of magnetic nanoparticles as external magnetic support and magnetic ILs (MILs) as easy to recover extraction media [14].

MILs have been introduced to the wider audience as a new subclass of ILs, which among many different applications appeared as interesting liquid extraction media for microextraction techniques. They are characterized by similar physicochemical properties as conventional ILs, but additionally, thanks to the introduction of a paramagnetic component to IL structure, they exhibit a strong response to external magnetic field. They have already found several applications in DLLME, where they can be easily retrieved after extraction by magnet-based platform, although their applicability is not focused mainly on aqueous samples. In fact, because of hydrophilic character and hydrolytic instability of the paramagnetic components, MILs have been initially successfully applied as extractants in hydrophobic matrices such as e.g. oils, but for the purpose of aqueous samples extraction, their structures had to be modified with hydrophobic groups [9]. The development of MILs is currently recognized somewhat as a breakthrough in ILs field, which deliver numerous opportunities for further evolution in different research areas, also in miniaturized modes of analytical chemistry.

HF-LPME is another microextraction technique which benefits from the application of ILs as extraction media instead of molecular solvents. Their tunable solubility and solvation power make them a reasonable alternative for rather narrow range of selection of low-polar or non-polar solvents typically used in HF-LPME. In addition, high viscosity of ILs reduces the risk of extraction phase loss from the HF segment while the sample is stirred vigorously. In the two-phase mode of this technique, ILs play a role of acceptor phase, whereas three-phase mode employs them as intermediate phase (trapped in the pores of the membrane) for preconcentration of the analytes [44,45].

The most often mentioned advantage of ILs in the context of their applicability as liquid (micro)extraction media, obviously next to their tunable properties (acidic/basic, hydrophilic/hydrophobic, water-miscible/water-immiscible), is negligible vapor pressure. This feature in turn appeared also as one of the major shortcomings in LPME techniques, because of the lack of direct compatibility with GC systems. The trials of enriched ILs injection into GC ended up with system contamination, which fostered a frequent maintenance [46]. Some solutions to this limitation have been already reported, based mainly on thermal desorption of the analytes from the enriched IL with the use of a special interface placed in the GC injection port [47,48] or simply by exposing the enriched drop of IL from the syringe needle tip in the injection port (which also allowed for IL retrieval after the process) [49]. Another reported solution involved the application of HS interface for introducing the analytes into GC system [50]. High viscosity of ILs may be also problematic when IL needs to be introduced into the system for final analysis. In order to provide compatibility with mobile phase or not to raise doubts about efficient introduction into measuring equipment, the addition of little amounts of organic solvents is sometimes required [51].

3.2. ILs as sorbents in sorbent-based microextraction techniques

The liquid state of ILs hinders their formation in stable, defined shapes. The implication of that is the difficulty in immobilizing ILs in/on analytical devices dedicated to sorption-based extraction techniques without losing their advantageous bulk properties. In order to apply ILs as extraction media in solid/stationary-phase − based microextraction techniques, ILs may be confined in or grafted to a supporting materials (forming in this way a hybrid material) or may be utilized in the form of polymeric ionic liquids (PILs) and PIL-based sorbents.

3.2.1. ILs-based hybrid materials

For obtaining a hybrid material, IL may be physically confined in the porous support by capillary forces or covalently grafted (chemically bonded) to the supporting material.

Physical confinement of ILs may be carried out by simple soaking of IL into pores of any type of supporting material (known as post impregnation) [52] or by synthesis of the supporting, porous material in the presence of IL (known as *in-situ* impregnation). In the latter case, a spatial solid structure with IL confined in the created pores is produced. In order to prepare a hybrid material by covalent grafting of IL to a supporting material, above methods may be also utilized, but additionally they are followed by washing out the unbound IL by an organic solvent (it is assumed that IL grafted to the supporting material surface is resistant to solvent treatment) [53]. Covalent grafting may be also proceeded by carrying out the reactions of cations with chemically active groups located on the supporting material surface [54].

The application of ILs covalently grafted to the supporting material is more often reported in the literature. The reason for this is their durability, which outmatches thermal and mechanical stability of physically confined ILs. Although it allows for taking the advantage of some native properties of ILs (e.g. low volatility), a chemical reaction between IL and supporting material results in the formation of a sorptive layer characterized by significantly modified sorption properties when compared to a native IL. As a result, in this form IL can no longer be treated as liquid [6]. On the other hand, ILs physically confined in the pores of different materials (e.g. silica [55], carbon nanotubes (CNTs) [56], metal-organic frameworks (MOFs) [57]) maintain their liquid-state sorption properties, and in addition, the IL-based hybrid system is characterized by improved thermal and mechanical stability, sorption capacity and selectivity towards specific analytes. Such systems where IL is kept confined, already successfully applied in several studies employing microextraction techniques, are gel-like hybrid materials, known from the literature as ionogels. The structures and properties of ionogels have been already widely investigated by several research groups [58,59]. It has been proved that confinement process may have a number of effects on obtained hybrid material, which play an important role in the context of physically confined ILs utilization as sorbents for microextraction techniques. For instance, the level of IL loading in the pores of the solid support has an impact on mechanical stability and diffusivity of the hybrid material. The higher the level of IL loading, the more stable is the shape of the material. On the other hand, if the pores are covered only with a thin IL layer, a decrease in mechanical stability may be observed, but diffusive limitations are significantly reduced. The properties of IL-based hybrid materials depend also on the structure of their interphase layers, strongly affected by the intermolecular interactions occurring between IL and the material. Strong interactions between IL and e.g. silica support lead to IL gathering in the area of its surface [60]. Depending on the IL distance from the surface, the contribution of bulk properties of ILs may change. These and other physical confinement effects on the properties of IL-based hybrid materials have been comprehensively reviewed in 2019 [57].

3.2.2. PILs and PILs-based sorbents

Polymeric ionic liquids (PILs) represent a different subclass of IL-based sorbents. They can be easily produced by the radical polymerization from IL monomers and crosslinkers. The properties of PILs may be tuned by the structure and amount of crosslinkers and substituents of IL monomers. By crosslinking the PIL with another polymer it is possible to obtain a highly specific surface area. The polymerization process may be also initiated at the specific surface by a grafting approach. The substrate is first functionalized by small groups which may further initiate the radical polymerization [61,62].

The application of PILs as sorbent coatings for SPME allows for benefiting from ILs tunable selectivity towards target analytes and overcoming several limitations of other IL-based sorbent coatings at the same time. PILs are characterized by high mechanical stability and higher viscosity in comparison to ILs so they do not flow from the fiber core during thermal desorption in GC injection port. In addition, PIL-based fiber coatings exhibit exceptionally good fiber lifetimes (around 150 extraction and desorption cycles). They may be also applied in both direct immersion and headspace SPME modes. It has been proved that the dominant extraction mechanism of PIL-based coatings is non-competitive partition, not affected by the presence of interferents in the sample, in contrast to e.g. commercially available PDMS/DVB coating [63]. All these factors made PILs an extremely popular source of SPME fiber coatings in recent years. Their applications in SPME technique have been already summarized in several review articles [64,65].

The developments in PIL-based sorbent coatings, which have been reported in the past few years, were mainly focused on improving the chemical, thermal and mechanical stability of PIL-based sorbents as well as enhancing their extraction capacity and selectivity towards target analytes in case of multi-component matrices. These incentives led to the introduction into SPME fiber coatings selection of PIL-based composites formed from PILs and other materials (several of them are listed below), which provided several additional properties of the resulting sorbents:

- multi-walled CNTs - enhancement of π-π interactions, improved extraction efficiency, durability and stability [66];
- polyaniline – large specific surface area, high enrichment capacity, high stability and durability [67];
- nitinol wires – good extraction performance under harsh matrix conditions (e.g. extreme pH) [68];
- nanoporous array anodic titanium – high surface-to-volume ratio, improved mechanical stability, enhanced hydrogen bond interactions [69].

4. Recent applications of ILs-based extraction media in microextraction techniques

ILs gained huge popularity among analytical chemists in the past decade. No wonder that next to numerous original papers reporting their various applications in sample preparation techniques available in the literature, there is also a significant number of review papers summarizing data in this topic. For this reason, in this review the relevant examples of ILs utilization in microextraction techniques reported only within past 5 years will be covered. We would like to draw the attention of the audience to the recent and diversified applications of ILs in LPME and sorbent-based microextraction techniques to give the overview on current trends in this field as well as some shortcomings which still need to be rectified.

4.1. Single drop microextraction

After its introduction into analytical practice over 20 years ago, single-drop microextraction (SDME) became one of the most popular solvent-based microextraction techniques as a practical sample preparation tool in chemical, biological, food, pharmaceutical, clinical and forensic analysis. Continued strong interest in SDME fostered new developments resulting in new technical solutions and the application of alternative to organic solvents extractants. Hydrophobic and hydrophilic ILs have found numerous applications in SDME, both in HS and DI modes [12]. The majority of most recent applications in turn employs MILs as SDME extractants. In MIL-based SDME a rod magnet serves for suspending the MIL directly in the aqueous sample or in its headspace of the extraction vial. By this solution, it is possible to suspend a higher microdroplet volume for prolonged sampling, even under strong stirring, in comparison to compared to other types of solvents (also conventional ILs) when using micro-syringes [70].

IL-based SDME has been recently applied in the analysis of environmental and food samples as well as in biomedical studies. Jahromi et al. [71], in their study dedicated to food analysis, utilized hydrophobic tetrachloromanganate (II)-containing MILs, exhibiting satisfactory magnetic susceptibility and acceptable production costs, in order to extract ascorbic acid from vitamin C and orange juice samples before its voltammetric detection. A single drop with only a micro-amount of an MIL acted as the extraction solvent, which was further exposed directly on the surface of the working electrode. The MIL-SDME-based extraction step acted also as a cleanup that eliminated interfering species in the electrochemical transduction and therefore improved the selectivity of the method. In the same year, Trujillo-Rodriguez et al. [72] applied MIL-based SDME in order to isolate short chain free fatty acids (SCFFAs) from milk samples. In this study however, the authors applied HS mode under reduced pressure during sampling. The application of MILs in such solution is supported by their resistance to vacuum - the air evacuation from the extraction vial can be achieved without risking the stability of the MIL micro-droplet. For this reason, this study is the first reported on the use of a vacuum-assisted LPME method. Worth to mention is, that equilibrium was reached faster than within regular atmospheric pressure MIL-HS-SDME and that the method does not require the derivatization of FFAs.

MIL-HS-SDME technique has been also recently applied by Fernandez et al. [73] in the study on chlorobenzenes isolation from water samples. The authors reported the first utilization of a hydrophilic $[C_2C_1IM]_2$ $[Co(NCS)_4]$ IL in such study. Worth emphasizing is the fact that in comparison to other previously reported analytical solutions, the MIL-HS-SDME-based one allowed for obtaining comparable or even lower LOD values in shorter extraction times. An et al. also reported the MIL-HS-SDME technique utilization for environmental analysis, but his work in turn involved also the comparison of applied solution with DLLME approach employing the same tetrachloromanganate-MILs. These two approaches have been tested on the extraction process of aromatic compounds from water samples. The authors confirmed the great advantage of MILs for HS-SDME purposes, namely highly stable microdroplet under elevated temperatures and long extraction times. They also emphasized another advantage of $[MnCl_4]^{2-}$ – based MILs – their low UV absorbance allows for the direct coupling to HPLC analysis [74].

MIL–SDME-based methodologies have been also recently applied to biomolecules isolation in biomedical studies. Magneto-active extraction is one of the often applied methods of DNA purification before PCR. However the application of traditional magnetic beads may pose a problem for subsequent PCR, namely its inhibition, if applied chemical reagents are incompletely removed. DNA may also insufficiently extracted by the beads because of their tendency to sediment and aggregate. For this reason, MIL-based microextraction appeared as a good solution to above mentioned problems. Emaus et al. [75] developed a methodology based on MIL-DI-SDME dedicated to short cell-free DNA fragments isolation before direct qPCR amplification. DNA-enriched hydrophobic MILs could be directly incorporated into reaction systems, without the need of time-consuming DNA recovery from extraction phase, and, worth emphasizing, no impact on amplification efficiency was observed. The methodology was tested on isolation and direct qPCR amplification of mutation prone-*KRAS* oncogene fragment in plasma samples. Similarly Ding et al. [76] benefited from extraction performance of hydrophobic MILs and their compatibility with reaction system in the study on DNA isolation from complex biological samples before isothermal nucleic acid amplification (INAA) aimed at detection of pathogens. A drop of hydrophobic MIL has been used for rapid DNA preconcentration from cell lysate and further added directly to the reaction mixture for amplification by INAA techniques. Above mentioned examples have a tremendous potential towards on-site analysis, indicated recently as one of the trends in modern analytical chemistry.

A shortcoming of MILs, mentioned in several works, is their limited thermal stability, which results in the lack of possibility to increase the analyte signal intensity during HS analysis or thermal desorption. This is an especially important factor, if one wants to avoid the dilution of MIL drop or a back-extraction procedure before instrumental analysis.

There are also several recent examples of non-magnetic ILs application in SDME-based analytical methodologies [77,78]. In these studies, ILs are modified with task-specific nanomaterials, e.g. nanocellulose (NC), CNTs, ZnO-nanofluid, in order to enhance the extractability of target analytes and support the formation of stable droplets. For instance, ternary composites of NC, CNTs and [BMIM] $[PF_6]$ IL, reported by Ruiz-Palomero et al. [41] as extraction phase for DI-SDME, exhibited an outstanding and selective ability for the preconcentration of the mutagenic 2-amino-3,8-dimethylimidazo [4,5-f]-quinoxaline, one of the heterocyclic amines, which is known as exceptionally problematic (due to its polarity) for isolation by unmodified ILs or organic solvents.

4.2. Dispersive liquid-liquid microextraction

Classical dispersive liquid-liquid microextraction (DLLME) was firstly proposed in 2006 by Rezaee and co-workers [79] as microextraction technique based on a ternary component solvent system composed of extractant, disperser and aqueous sample, which after extraction process is separated by centrifugation. The first application of ILs as extraction solvents in DLLME technique was performed in 2008 by Zhou et al. [41]. From that time ILs have been extensively utilized in DLLME for the extraction and preconcentration of a wide variety of organic and inorganic analytes in environmental, food and biomedical studies. In the majority of the reported applications, hydrophobic ILs were employed as extraction solvents. However, hydrophilic ILs also found several applications in the *in situ* mode of DLLME technique, which has been discussed and referenced in the previous section. A huge interest of scientific community in ILs utilization in DLLME technique has led to numerous research papers reporting both different analytical applications and novel technical solutions in this topic. These data has been summarized in several review papers. Trujillo-Rodriguez et al. [45] focused on four main modes of ILs-based DLLME, namely (i) conventional IL-DLLME; (ii) temperature-controlled IL-DLLME; (iii) ultrasound/microwave/vortex-assisted IL-DLLME; and (iv) *in-situ* IL-DLLME. Rykowska et al. in turn, in recently published review paper [14], points the audience attention to latest alterations and novel approaches in ILs-based DLLME: (i) magnetic retrieval IL-DLLME; (ii) magnetic effervescent tablet-assisted IL-DLLME; (iii) MIL-DLLME. In this work, magnetic retrieval of ILs after extraction process is clearly indicated as one of the noticeable trends and MILs application in LPME techniques is described as an evident hot topic. The review of Rykowska et al. comprehensively covers the latest trends in ILs application in DLLME technique and includes relevant literature examples published up to 2017. For this reason, in this review we decided to focus on most recently reported applications of IL-DLLME technique and works published in the past two years will be referenced.

In-situ IL-DLLME has been recently applied by Zhang et al. [50] for trace amounts of PCBs (low ppt level) and acrylamide (low

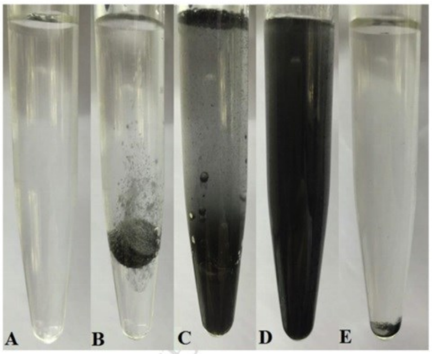

Fig. 5. The steps of extraction by magnetic effervescent tablet-assisted IL-DLLME technique: a) thermostating of the sample; b-c) placing the effervescent tablet in the sample and initiation of the effervescence reaction; d) homogenous distribution of the extraction solvent; e) concentrating the MNPs with enriched IL at the bottom of the vial [85]. Copyright 2016 by Elsevier.

ppb level) isolation from milk and coffee samples. The enriched IL was analyzed by HS-GC instrument. The authors reported satisfactory metrological parameters and good matrix compatibility of the developed methodology.

Solution similar to the *in-situ* mode has been applied by Pacheco-Fernandez et al. [80] in order to isolate hydroxylated PAHs from urine samples. The authors applied ($[C_{10}Gu^+][Cl]$ IL as extractant in salt-induced DLLME, which principle also lies in promoting the insolubility of IL in the sample (as in case of *in-situ* mode), but this has been achieved by $NaClO_4$, excluding in this way the use of toxic fluorine-based salts, often applied in *in-situ* IL-DLLME. However, it should be mentioned that perchlorate is considered by USEPA as potentially harmful to human health and ecosystems.

Fan et al. applied IL-DLLME in *in-situ* mode together with ultra-small Fe_3O_4 magnetic nanoparticles in order to extract pyrethroid pesticides in water samples. Such approach is called *in-situ* IL-DLLME with magnetic retrieval (*in-situ* MR-IL-DLLME). It's principle is based on retrieval of the *in-situ* formed IL by magnetic nanoparticles Fe_3O_4. For enrichment of pyrethroids from water samples, hydrophilic IL $[P_{4448}][Br]$ was applied, which further reacted *in-situ* with anion-exchange reagent Na $[N(CN)_2]$ forming hydrophobic IL. Collection of enriched IL was supported by superparamagnetic Fe_3O_4 nanoparticles. The authors indicated their method as nanometer-level microextraction with additional advantages of being easy-to-perform, rapid and sensitive [81].

Another novel solution in IL-DLLME technique called effervescence assisted IL-DLLME (EA-IL-DLLME) is based on effective dispersion chemically assisted by the effervescent reaction, without the need of dispersive solvent addition. By combining effervescence reaction and magnetic retrieval of enriched IL, another mode of IL-DLLME has been formed, namely magnetic effervescent tablet-assisted IL-DLLME. In this case, the magnetic nanoparticles are introduced into the sample in the form of effervescent tablet together with IL (Fig. 5) [82].

The combination of effervescence dispersion and magnetic recovery provides convenient retrieval of IL and effective dispersion chemically assisted by the effervescent reaction. The effervescent dispersion was applied by Wu et al. [83] in the development of an analytical procedure dedicated to acaricides determination in honey and tea samples. The authors used IL-based TiO_2 nanofluid, which facilitates superior dispersion stability. The IL-based nanofluid was used to form effervescent tablet together with sodium dihydrogen phosphate dihydrate and anhydrous sodium carbonate. After the addition of the tablet into the sample, the effervescence immediately occurred and fine droplets of the extraction phase were homogeneously distributed in the sample solution with the assistance of formed carbon dioxide. The authors described their methodology with several advantages: short extraction time, high recovery, high enrichment factor, low consumption of organic solvents and ease of operation.

De Boeck et al. [84] proved the applicability of IL-DLLME technique for selective isolation of trace levels of target analytes from samples characterized by complex matrix composition and high concentrations of interferents without prior sample pre-treatment. The authors extracted 19 antidepressants from the whole blood sample by 60 µl of 1-butyl-3-methylimidazolium hexafluorophosphate, which were further detected and quantified by LC-MS/MS system.

An increasing number of papers published within the past few years have reported MIL-DLLME methodologies, which is not surprising, taking into consideration the recently observed growing interest in application of MILs in LPME techniques. Most recently developed MIL-DLLME procedures are dedicated to determination of biomolecules in biological samples, e.g. DNA isolation [85,86], extraction of viable *E. coli* cells from aqueous solutions [87], extraction of the hormones estriol and extrone from urine samples [88].

MILs were also applied as extractants in modified version of DLLME – stir bar dispersive liquid microextraction (SBDLME). In this solution, MIL was dispersed by a Nd-core magnetic stir bar as fine microdroplets. When the stirring was stopped, the enriched MIL was collected by the stir bar due to its magnetic attraction. Such approach has been applied to PAHs isolation from water samples [89].

4.3. Solid-phase microextraction

Solid-phase microextraction (SPME), introduced by Pawliszyn and his co-workers almost 30 years ago, is so far one of the most often applied solvent-free microextraction techniques for sampling and preconcentration of analytes from environmental, food and biological samples. Extending the scope of SPME applicability fostered the development of new sorbents, which could fill the gap in the rather narrow selection of commercially available fiber coatings. Recent findings in the field of coating materials for SPME has been reviewed in 2017 [90]. ILs-based sorbents emerged as a promising alternative in 2005, when disposable IL coating has been tested for the first time in headspace SPME of benzene, toluene, ethylbenzene, and xylenes from paints [91]. From that time, the scientists tested numerous approaches to immobilize ILs in the form of thermally and mechanically stable fiber coatings with controllable coating film thickness [92]. Next to dipping and agglutinating methods, which did not allow for the preparation of fibers of satisfactory durability and reproducibility, methodologies such as sol-gel technology, surface-modification techniques, electrochemical methods and liquid-phase deposition in case of in-tube SPME appeared to produce diverse and stable coatings.

Sol-gel methodology allows for obtaining a hybrid organic/inorganic network by formation of a "sol" solution followed by a gelation process in the presence of IL to form a network, in which IL is confined [93]. Obtained in this way material is called an ionogel. Ionogels are non-leaching IL-containing materials, in which liquid-like nature of ILs is kept. Pena-Pereira et al. reported in 2014 [94] and 2015 [95] the utilization of ionogels as fiber coatings for the isolation of organic pollutants from water samples by HS-SPME technique. The authors confined high loadings of [TFSI]-based ILs in three-dimensional silica network. The fibers prepared from $[C_4C_1IM][TFSI]$ and $[C_4C_1Pyrr][TFSI]$ ILs were proved to exhibit satisfactory extractability of studied aromatic and chlorinated VOCs and remarkable durability of respectively 60 and 100 consecutive analytical cycles, without visible decline in extraction performance. Ionogel-based fiber coatings were also evaluated by Pang et al., in 2016 [96]. The authors fabricated hybrid silica-based materials with immobilized $[C_{16}C_1IM][TFSI]$ IL and applied them as fiber coatings for the extraction of organophosphate esters from water samples by HS-SPME. The evaluation of tested fibers lifetime resulted in 4–21% deterioration in response signals after 40 times of extraction-desorption cycles. In all above mentioned studies, the authors declared superior extraction performance in comparison to commercially available coatings. This is related to high loadings of ILs in the porous network which provided enhanced extraction capacity.

Another recently reported materials for the fabrication of stable IL-based fiber coatings, which were obtained by IL immobilization in a porous structure, were MOF-based hybrid materials [97]. The fiber coating material was prepared by *in-situ* growth of isoreticular MOFs on stainless steel wires, which were further immersed in $[C_4C_1IM][PF_6]$ IL and protected by PDMS layer. Fabricated fiber coatings were characterized by porous structure, increased surface-to-volume ratio and long lifetime, reaching up to 100 analytical cycles. Their applicability was successfully tested in the study of HS-SPME isolation of polycyclic aromatic hydrocarbons (PAHs) from rainwater samples. The wider applicability of isoreticular MOFs is limited by their high moisture sensitivity and poor thermal resistance. In the mentioned research, the authors solved this problem by coating the MOFs with IL and PDMS. The IL played not only the role of extraction phase, but also prevented the material from substantial cracking caused by moisture, PDMS layer in turn provided a remarkable resistance to high temperature and humidity. In order to avoid the mentioned risks, MOFs may be replaced by porous aromatic frameworks (PAFs), which exhibit high moisture and chemical stability. This solution has been applied by Wu et al. [98], who reported in 2016 a novel hybrid material produced from 1-(triethoxysilyl)-propyl-3-aminopropylimidazole hexafluorophosphate IL and PAFs, which was further used as SPME fiber coating. The fiber applicability was tested in the study of organochlorine pesticides (OCPs) isolation from water samples. A high adsorption capacity, provided by porous structure of functionalized PAFs, π-π interactions between both analytes-PAFs and analytes-IL and electrostatic interactions between IM-based cations and OCPs. PAFs/IL-based fibers were used for over 100 extraction-desorption cycles without a significant decrease in extraction performance.

Numerous novel ILs-based fibers dedicated to SPME technique reported recently in the literature were obtained by surface-modification methodologies as well as electropolymerization. These techniques allow for the precise fabrication of advanced, highly durable and robust (also in case of DI-SPME applications), multi-component structures, which prove that a huge step forward in the development of alternative SPME fiber coatings has been made in the past few years.

As a good example, the crosslinked PIL-based coatings chemically bonded to nitinol supports, obtained by Ho et al., in 2014 [71] may be given. The fibers were fabricated in a two-step methodology: (1) a nitinol wire was first oxidized and then derivatized by vinyltrimethoxysilane – as a result, vinyl groups were attached to the surface of the support; (2) PIL-based network covalently attached to the wire was obtained by UV-initiated on-fiber copolymerization of the vinyl-modified nitinol support with IL monomers ([VC$_6$IM][Cl], [VC$_{16}$IM][TFSI] and [VBC$_{16}$IM][TFSI]) and IL crosslinkers. The aim of the authors was to take advantage of remarkable elasticity and tensile strength of nitinol wires and high PILs selectivity and robustness in order to produce a novel ILs-based SPME fiber coating representing a good extraction efficiency under even harsh extraction conditions. Extraction studies on model solutions of extreme pH, high temperatures and after pre-exposure to organic solvents, resulted in satisfactory precision and extraction efficiency. Fabricated fibers were also tested in the case study of phthalate esters isolation from drip-brewed hot coffee by SPME in DI mode. In this case the authors also obtained satisfactory analytical performance and, in addition, they could use the fibers over 70 times, even under harsh conditions applied during the research.

Modified nitinol wires were also applied as supporting materials for ILs-based sorbents in the recently reported study of An and Anderson [99]. Following the work of Feng et al. [100], the authors used styrenesulfonate counterion-based IL to prepare a double-confined PIL-based sorbent, characterized by high robustness, stability and resistance to undesired ion exchange process occurring in case of DI-SPME mode in the solutions of high ionic strength. The IL-monomer ([VImC10][SS]) and crosslinker ([(VBIm)$_2$C$_{12}$] 2 [SS]) were coated onto the modified nitinol surface and co-polymerized. The fabricated fiber coatings were highly reproducible and exhibited good analytical performance as well as extended (in comparison to other PIL-based coatings and commercially available ones) lifetime when tested for the isolation of UV filters by DI-SPME from aqueous samples of high salt concentration.

Several reported recently in the literature examples of novel, mechanically and chemically stable as well as highly porous (with increased surface area) SPME fiber coatings were produced by electrochemical polymerization of conducting polymers. This method allows for fabricating the coating of easily controllable film thickness and high quality, which strongly adheres to the support material. Conductive polymers, applied in the past few years for the formation of IL-based SPME fiber coatings, are: polythiophene (PTh) [101], polyaniline (PANI) [102] and polypyrrole (PPy) [103]. The physicochemical properties of the polymers were tuned by the IL moieties which was followed by coating the surface by electropolymerization. Prepared conductive PILs (CPILs) – based films were robust and highly selective, thus perfect for microextraction. Pelit et al. [104] intercalated different ILs with IM-based cations and [Br] anion within the structure of montmorillonite clay, co-deposited the materials with polythiophene polymer and coated electrochemically on a SPME fiber. Fabricated coatings were tested as sorption materials for endocrine disruptor pesticides present in fruit juice samples. Li et al. [66] prepared a three-dimensional porous material composed of MWCNTs, graphene oxide and [(HO–C$_2$)C$_1$IM][BF$_4$] IL and co-electrodeposited it with PANI on stainless steel wire. This fiber was applied for the isolation of alcohols from tea drinks. Devasurendra et al. [105] covalently bonded pyrrole to [C$_6$MIM]-based IL, doped it with single wall CNTs and electropolymerized on platinum wires. The fiber coatings were tested in isolation of FAMEs and aromatic compounds from aqueous samples. In all above mentioned examples, HS-SPME mode was applied. All authors reported high fiber-to-fiber reproducibility and thermal stability, long lifespan and selectivity towards polar analytes provided by conductive polymers. Moreover, it has been also stated in above mentioned works, that the utilization of additional supporting materials such as montmorillonite clay and CNTs, provided additional specific interactions enhancing the extractability of target analytes. For instance, improved extraction efficiency of CNTs-based coatings towards aromatic compounds is provided by π-π interactions [105], whereas the modification of the clay with ILs altered the surface morphology and therefore the adsorption capacity of the coatings, providing a dual character of IL-clay material. A non-polar character of alkyl chain next to ionic structure of the clay ensured a satisfactory extraction efficiency of target analytes characterized by different polarities [104].

Mentioned above study of Li et al. [66] is a good example of recently observed trend in fabrication of ILs-based SPME fiber coatings, which benefit not only from unique properties of ILs but also of highly advantageous features of nanomaterials. These are: (i) large specific surface area; (ii) multiple active sites; (iii) ability to form specific interactions with analytes; (iv) mechanical, chemical and thermal stability. Thanks to the synergistic physicochemical properties, analytical extraction by ILs-nanomaterials hybrids turned out to be highly selective. Next to CNTs, which are most often applied nanomaterials for the preparation of SPME fiber coatings, graphene oxide (GO) has been also utilized for this purpose [104]. GO is characterized by higher surface area in comparison to CNTs, it is also a better choice for extracting polar analytes because of the ability to form hydrogen bonding or electrostatic interactions. Sun et al. [106] took the advantage of GO and used it for the fabrication of PIL monolith-based SPME device. GO-PILs sorbent exhibited satisfactory extraction efficiency towards phenolic compounds present in water samples in DI-SPME mode. However, carried out extraction studies also revealed the possible undesired competition between the analytes and water molecules,

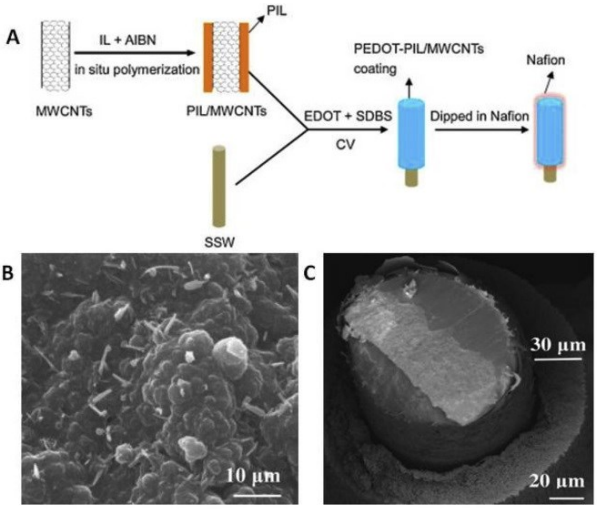

Fig. 6. The example of multi-component IL-based SPME fiber: a) steps of fiber fabrication; b) surface SEM image of the fiber of nodular accumulating structure with scattered MWCNTs; b) cross-section SEM image of the fiber [107] (Copyright 2016 by Elsevier).

which may limit the adsorption of target compounds on the surface of hydrophilic character.

As a summarizing of given so far literature examples on ILs-based SPME fiber coatings it may be stated that there is a visible trend of combining several mentioned above strategies to fabricate new and highly selective fibers and move the border of their applicability towards complex samples and demanding extraction conditions. For instance, for the fabrication of a fiber coating dedicated to highly selective isolation of carbamate pesticides by DI-SPME from fruit and vegetable samples, PILs, nanomaterials (MWCNTs), conductive polymer for subsequent electro-polymerization (3,4-ethylenedioxythiophene) and Nafion for the coating surface modification were utilized (Fig. 6) [66]. With the utilization of the produced fiber, the analytes could be quantitatively recovered and determined at a ppb level. The fiber could be used for around 150 extraction-desorption cycles and no deterioration in obtained signal was observed.

ILs-based sorbents may be utilized also in modified versions of classical SPME, namely in-tube SPME and hollow-fiber SPME (HF-SPME).

In-tube SPME was introduced by Pawliszyn et al., in 1997 [105] as an extraction technique applying a specially designed device, e.g. fused silica capillary or polyether ether ketone (PEEK) tube modified with sorption materials, coupled to HPLC, dedicated to on-line analysis. Recently reported in the literature applications of this modification of SPME technique involve PILs as coating materials. For this purpose PILs were immobilized in the device by (i) coating the stainless steel wire with the PIL and packing it into the PEEK tube [106]; (ii) grafting the PIL onto basalt fibers (with the aim of improved durability) and similarly packing it into PEEK tube [107]; (iii) coating the walls of open tubular capillary column with PIL [108]. Each solution has been proved to produce mechanically and chemically stable sorption phases, suitable to be incorporated into on-line monitoring systems dedicated to e.g. PAHs determination in soil samples or endocannabinoids in plasma samples. It has been however emphasized, that the fabrication of fiber-in-tube SPME devices involves more steps in comparison to coating the open tubular capillary [111].

HF-SPME is a hybrid of HF-LPME and SPME, were hollow-fiber membrane contractors providing mass-transfer between two phases without the dispersion of one phase in another is filled with a solid phase. There are not many examples of such SPME modes in the literature. In addition, if ILs are applied as hollow-fibers “fillers”, such approach is typically counted as HF-LPME example. However, recently so called “frozen” ILs, with an example of $[C_{16}MIM][TFSI]$, which are solids under ambient temperature and highly hydrophobic, were applied as hollow fiber filling agents and the approach was classified as HF-SPME [109]. “Frozen” IL confined in pores of a hollow fiber efficiently extracted DDT and its main metabolites from water samples.

Finally, the examples of highly demanding extractions of DNA and RNA from complex biological samples, which have been significantly facilitated in recent years by the application of PIL-based SPME should be given. SPME approach appeared as a reasonable alternative to LLE and SPE techniques, being more effective, convenient, time-saving, solventless and reusable. Nacham et al. [110,111] reported the highest extraction efficiency towards nucleic acids was exhibited by the fiber fabricated from $[V(C_9COOH)IM][Br]$ IL monomer and the $[(VIM)_2C_{12}]_2$ [Br] IL crosslinker. The authors indicated electrostatic interactions and ion-exchange as the dominant mechanisms of nucleic acids enhanced extractability by the ILs-based fiber coatings. Similar improved DNA extraction performance by PIL-based SPME fiber coatings was reported by Varona et al. [112]. The great potential of above mentioned approaches lies not only in the certain “laboratory” advantages of SPME over LLE and SPE, but also in the possibility of creating SPME-based purification platforms for recently highly valued point-of-care diagnostics.

4.4. Dispersive sorption-based techniques

In order to carry out SPE in miniaturized mode, a solid phase may be dispersed in an liquidous sample. This provides a significant enhancement of interactions between the two phases, therefore the extraction lasts significantly shorter than during classical SPE and on top of that, organic solvent consumption is significantly reduced. In other words, this approach is called dispersive solid-phase microextraction (micro-SPE or D-μSPE). Reported in recent years examples of the combination of this technique with ILs as sorbents have been somewhat dominated by ILs-nanomaterials hybrids. The obvious advantages of nanosized sorbents which appeared to be suitable carriers for ILs in micro-SPE are large surface area and short diffusion route, providing improved extraction dynamics, therefore high extraction efficiency, and ease of surface functionalization/modification [113].

The greatest interest in micro-SPE applications has been gained by nanoscale carbon-based materials. Several recently reported applications of ILs-based nanoscale sorbents in micro-SPE involved the use of CNTs, carbon nanospheres (CNSs), GO and MOFs. CNs coated by [NMIIM][Br] has been recently used for the preconcentration of Cu (II) and Pb (II) ions [114] from aqueous (sea water, wastewater) and solid (street dust, spices) samples. It has been proved that the methodology is resilient towards the addition of other monovalent and divalent metal ions. After eight subsequent extractions, adsorption performance loss was observed and CNs had to be re-coated. This may cause an inconvenience, but it should be pointed out that very little amount of ILs is used for a single coating. GO and its unique properties has been already described in SPME section. No wonder that it has been also applied as a carrier for ILs in dispersive micro-SPE in order to fabricate advanced sorbents with tunable extractabilities. In the recent study of Serrano et al. [115] IL covalently attached to GO sheets was utilized as the extraction phase for anabolic steroids and β-blockers isolation from aqueous samples by dispersive micro-SPE technique. The authors reported that the material could be re-used for at least three consecutive extractions without a visible deterioration of efficiency.

Novel ILs-based sorbents dedicated to d-SPE have been also fabricated from MOFs nanoparticles [116], benefiting from their ultrahigh surface area, high dispersion stability and hydrophilicity. To overcome their serious limitation related to water stability and toxicity, MOF-based materials modified with stable and functional groups, e.g. MIL-100(Fe) - synthesized by connecting FeO clusters with benzenetricarboxylic acid as the organic linker, appeared as a good alternative in extractions in aqueous solutions. The introduction of [BMIM][Cys] IL into the ordered structure of MOFs allowed for obtaining a nanoscale sorbent of high adsorption capacity and fast sorption of PAHs present in environmental water samples, vegetable and fruit juices. The adsorption properties of IL-MIL-100(Fe) sorbent towards PAHs are governed by stabilizing effect of ʟ-cysteine to π system which facilitates the interaction between IL-modified sorbent and target analytes.

The attractiveness of nanosized sorbents application in dispersive micro-SPE is supported by the availability of nanomaterials characterized by large constant magnetic moments – magnetic nanoparticles (MNPs). MNPs can be easily collected by using an external magnetic field placed outside of the extraction vial without additional centrifugation or filtration of the sample, which makes sampling and collection simplier and faster [116]. The possibility to modify MNPs with ILs resulted in numerous applications of ILs-based dispersive magnetic SPE (d-MSPE) technique.

Recently widely exploited GO has been also applied as magnetic support, onto which double-charged IL was covalently bonded, forming in this way a novel, magnetically separable sorbent [117]. It has been applied for ultrasound-assisted (USA) simultaneous separation and preconcentration of Pb(II), Cd(II), Ni(II), Cu(II) and Cr(III) from medicine capsules. No interference has been observed in the presence of other metal ions. The sorbent exhibited satisfactory reusability for eight subsequent extractions. The loss in extraction performance was explained by the authors by the alterations in IL-based coating as well as by the loss of magnetic properties after subjecting the particles to the US and elution by acidic solution – as a result a magnet couldn't remove the particles completely for further analytes recovery. An interesting solution for d-MSPE has been recently reported by Liu et al. [118], who fabricated and applied as a magnetically separated nanoscale sorbents IL-coated and cyclodextrin functionalized magnetic core dendrimer nanocomposites. Dendrimers are monodispersed, highly branched, and symmetrical polymers with a high density of functional groups. Because of their three-dimensional structure and high density of surface groups, they can be utilized as hosts for wide range of molecules and ions. The molecules may be either confined in the interior of dendrimers or bonded/adsorbed on their multivalent surface. Thanks to the multiplicity of surface groups, it is also possible to modify the material with the aim of its task-specific functionalization [119]. Reported in the study of Liu et al. [121] nanocomposites fabricated from inorganic magnetic nanoparticles, cyclodextrin-functionalized dendrimers and ILs, where the latter two exhibit the ability of selective preconcentration of target molecules, appeared as a powerful tool in highly efficient, fast and convenient methodology of pyrethroid residues determination in juice samples. Cyclodextrin provide high supramolecular recognition capability which is obtained by the formation of host–guest inclusion complexes between cyclodextrin and pyrethroids. ILs increased its extraction efficiency and, in addition, acted as a surfactant accelerating the mass transfer between analytes and adsorbents. Multi-component nanocomposites have been also applied in other study dedicated to developing new sorbents for selective isolation of pesticides from juice samples. Yang et al. [120], by one-pot method, fabricated a magnetic sorbent composed of (i) Fe_3O_4 nanoparticles – to provide magnetic properties and facilitate phase separation; (ii) conducting polymers (PANI and PPy) – to enhance adsorption ability; (iii) attapulgite – to benefit from two-dimensional structure and heterogeneous deposition of carbonaceous species on its surface; (iv) ILs – to provide selective extraction and surfactant activity (hemimicelles formation). These magnetic nanoparticles-based mixed hemimicelles have been applied in a modified version of d-MSPE, namely mixed hemimicelles solid-phase extraction (MHSPE) of acaricides isolation from juice samples. The authors reported a high extraction efficiency of the synthesized sorbent, but it could be re-used without the significant loss in performance only four times.

4.5. Other sorptive techniques

There are several scientific articles published recently reporting the application of ILs-based sorbents in techniques other than SPME and micro-SPE.

Stir-bar sorptive extraction (SBSE) has been proposed to overcome the problem of limited extraction capacity and fragile fiber coatings, often encountered in case of SPME. The limited selection of commercially available stir bar coatings (PDMS, EG-silicone, PA) led to the increased interest in the development of coatings with high affinity towards polar analytes [121]. In 2014 Fan et al. [122] reported for the first time the fabrication of ILs-based stir-bar

coating. The coating was produced by chemical bonding of ([AIM][BF_4]) IL to the stir-bar surface *via* sol-gel technology. The sorbent exhibited good mechanical strength as well as thermal (up to 360°C) and chemical (organic solvents, acid, alkali) resistance. The authors tested the sorbent in extraction process of nonsteroidal anti-inflammatory drugs (NSAIDs) from water, urine and milk samples and obtained high enrichment factors towards target analytes. In subsequent years, PILs-based sorbents have been applied as monolithic cakes in modified version of SPE – stir cake sorptive extraction (SCSE). In comparison to its "mother" technique, SCSE is more convenient and cost-effective as the lifespan of the cake is significantly longer. This is due the fact, the monolithic cake is not in acontact with the vessel wall during stirring and there is no friction loss of extraction medium. PIL-based SCSE has been recently applied by Chen et al. for determination of estrogens in environmental samples [123] and preservatives in beverages [124]. In both cases 1-ally-3-vinylimidazolium chloride has been used for the synthesis of PIL. Obtained satisfactory extraction performances of estrogens with polar hydroxyl groups and hydrophobic phenyl groups as well as preservatives being polar compounds have been provided by the multiplicity of interactions ($\pi-\pi$, hydrophobic, hydrogen-bonding and dipole–dipole) between utilized PIL and target analytes.

Another sorption-based extraction technique, somewhat similar to SBSE and SCSE, in which ILs-based sorbents have been recently utilized, is rotating-disk sorptive extractions (RDSE). Fiscal-Ladino et al. [125] intercalated [HDMIM][Br] IL into galleries of montmorillonite clays and loaded the fabricated sorbent into the cavity on one of the Teflon disk (containing an embedded miniature magnetic stirring bar) surfaces. The hydrophobicity of the hexadecyl moiety provided efficient extraction of polychlorinated biphenyls (PCBs) from water samples.

There are also very recent examples of PILs application in specifically designed devices dedicated to microextraction: fused silica capillary with inside-synthesized PIL-based monoliths [126] and portable tip microextraction device [127].

5. Conclusions

The challenges that analytical chemists face currently, i.e. trace analysis of samples characterized by complex matrix composition such as e.g. biological ones, demand for "green" approaches and specific solutions for e.g. point-of-care diagnostics, the trend of miniaturization and lowering the costs of single analytical cycle, fostered the implementation of ILs with their unique properties, known for many years as designer solvents. It goes without saying that ILs play currently an important role in analytical chemistry and they are exploited in many different ways for the purposes of chemical analysis. Sample preparation is one of the fields, where most recent innovations are related to the application of ILs as solvents in liquid-phase (micro)extraction and sorbents in solid-phase (micro)extraction. Microextraction techniques mostly dominated in the past few years by ILs implementation as extractants are DLLME and SPME. Especially in case of novel solutions in SPME, ILs are often incorporated into multi-component, task-specific hybrid sorbents, in which each component play a defined role in extraction process. In many of reported studies, ILs-based extraction media exhibited better extraction efficiencies towards target analytes in comparison to organic solvents or commercially available sorbents. However, still many of the ILs-based sorbents lack durability while applied in DI-SPME mode. It should be also emphasized that a huge advance has been made in the isolation of biomolecules by ILs-based extractants. It is expected that they will be further exploited in bioanalysis.

The number of applications of MILs in microextraction techniques increases significantly year by year, which has been recognized as a hot topic opening new possibilities in sample preparation. MILs, with their excellent response to external magnetic field, have attracted the interest of analytical chemists as the replacements for non-magnetic solvents, especially in case of DLLME technique. MILs opened new possibilities in LPME techniques, for instance they may be applied in vacuum LPME. Further investigation in MILs with better thermal properties seems necessary for extending their applicability to less volatile analytes.

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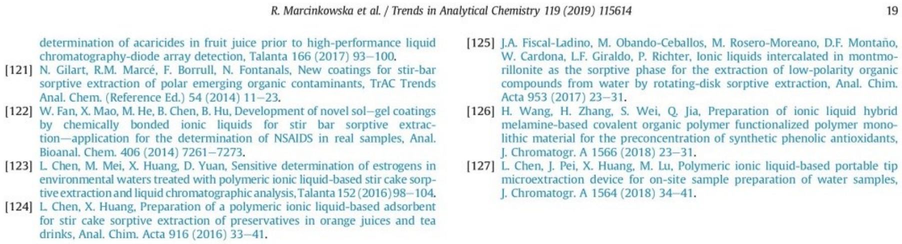

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Załącznik 2

Porous material-based sorbent coatings in solid-phase microextraction technique: Recent trends and future perspectives

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Porous material-based sorbent coatings in solid-phase microextraction technique: Recent trends and future perspectives

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ABSTRACT

The use of porous materials as sorbents in sample preparation techniques has gained recent scientific attention in the context of developing novel fibers for the Solid-phase microextraction (SPME) technique. SPME requires the appropriate selection of a robust sorbent for successful utilization under variable conditions. A deeper understanding of the nature of newly developed porous SPME coatings and the impact of their structures on their analytical parameters is crucial for ensuring their successful use as potential sorption media for specific purposes. This review presents a thorough discussion of currently popular SPME-based porous materials in the context of their structures.

1. Introduction

The determination of trace-level analytes in samples with a complex matrix composition (e.g., biological or contaminated samples) is often an integral part of environmental assessment and monitoring and analytical research of environmental pollutants. The sample preparation step is crucial for ensuring the accuracy and reliability of results obtained from analytical procedures. The principles of green analytical chemistry (GAC) necessitate the consideration of certain additional conditions; these principles have become a foundation for the development of new technical and methodological solutions. Solid-phase microextraction (SPME) is a popular analytical sample preparation technique that meets the requirements of GAC; SPME was developed in the 1990s by Prof. Janusz Pawliszyn, undergoing constant modes and fibers developing year by year (see Fig. 1) [1]. The SPME technique is extensively applied in analytical practice because it has several advantages over conventional extraction methods; SPME is relatively simple, rapid, solvent-free, sensitive, and provides linear results for a wide range of concentrations and analytes [2]. The SPME technique requires the appropriate selection of a robust sorbent for successful utilization under variable conditions. Porous materials have been particularly investigated as alternative sorbent coatings for SPME in response to these issues [3].

According to the International Union of Pure and Applied Chemistry (IUPAC), porous materials are defined as solids possessing pores, channels, cavities, or gaps whose depth is greater than their width [4]. Porous materials, such as zeolites [5] and silica gels [6], can be potentially applied in fields such as adsorption [7], catalysis [8,9], and nanotechnology [10], where their significant sorption properties can facilitate the separation of liquids and gases [11] and several other processes. The characteristics of porous materials vary depending on the size, arrangement, and shape of the pores, as well as the porosity (the ratio of the total pore volume relative to the apparent volume of the material) and composition of the material. Porous materials possess unique physical, thermal, morphological, and mechanical properties that enable their use in several applications [12]. The appropriate selection of porous materials as sorbent coatings depends on the analytes or the sample matrix being analyzed. As of extreme importance is to use the specific SPME coating towards specific analytes. The sampling of various compounds by SPME could be performed with the use of different kinds of commercial fibres, such as polydimethylsiloxane (PDMS), carboxen (CAR), divinylbenzene (DVB), Carbowax (CW), and Carbopack, as well as their mixtures [13].

The classification of SPME coatings is made into four categories, respectively, by the type of coating, by the coating thickness, by polarity, and depending on if the coating extraction mechanism is absorption or adsorption. The listing of the commercially available fibres, with specified extraction mechanisms and the coating's polarity were given by Pawliszyn in 1997 [1].

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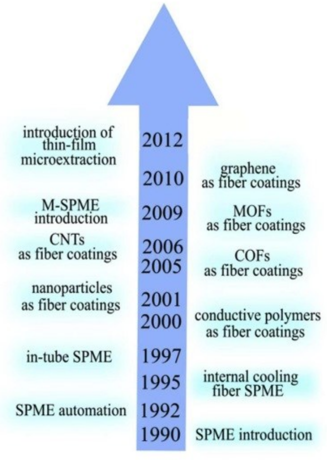

Fig. 1. Milestones of SPME technique development.

The polarity of a coating is determined by the type of the applied phase. Polarity can also determine the selectivity of the coating via enhancement of the affinity toward polar analytes, compared to that with nonpolar ones. Interestingly, the surface of the PDMS coating can reduce the overall polarity of the fiber; however, analytes can still be extracted in these cases through contact between the pores and polar analytes. Notably, the analyte capacity of the fiber is determined by the thickness of the coating, which can also provide information on the duration of extraction required for achieving equilibrium. Thicker coatings require a longer duration for achieving equilibrium. A thick coating retains volatile analytes, whereas thin coatings are preferred in the case of high-molecular-weight analytes [14].

Commercially available fibers for SPME possess coatings that are composed of polymeric materials, most of which operate on the basis of an adsorption mechanism. The adsorption mechanism can involve undesirable phenomena that limit the usefulness of the SPME technique; the phenomenon of competition in samples with complex compositions or limiting the linearity of the extraction process leads to a reduction in the extraction efficiency. These limitations can be overcome if materials in a liquid or “pseudo-liquid” state are considered; these materials enable the isolation of sample components through the absorption (partition) mechanism [15]. The features of the adsorption and absorption mechanisms are listed in Table 1.

Notably, PILs [16] or membranes (for membrane-based SPME or M-SPME) are also employed as absorbent-based coatings, wherein the shape of the cover is dependent on the PDMS-based protective membrane [17]. The problems related with the partition mechanisms, limited selectivity and the matrix influence can be solved with the porous coating of the SPME fiber. Thus, the fiber do not only fulfill the role of adsorbent, but also may constitute as the carrier or skeleton of the SPME fiber [18].

The main purpose of developing the SPME technique is to minimize or even lack the use of the organic solvent, reducing the extraction time and analyzed sample size. The selection of the SPME sorbent material is made based on the nature of the target analytes; thus, selecting appropriate coating material is of great importance in the SPME applications. It should also be emphasized that, proposed by researchers, new designs of the SPME sorbent coatings contribute to solving the problem with complexity related to diverse matrices determination.

Table 1
Advantages and limitations in the absorption and adsorption extraction mechanisms.

Extraction features	Absorption	Adsorption
Matrix influence	−	+
Wide range of the procedure linearity	+	−
Relatively low desorption temperatures	+	−
Interactions	weak	strong
Easiness in thermal desorption	+	−
Selectivity	−	+
The large surface area	−	+
High thermal and mechanical stability	−	+
Degradation of analytes during thermal desorption	−	+

The application of porous materials in SPME has attracted recent scientific attention. Several recent studies have confirmed their applications concerning environmental and biological samples [19], studies concerning the applications of MOFs [20]; magnetic sorbents [21]; and sorbent-based headspace extractions [22]. Additionally, the critical evaluation of the SPME sorbent materials [23] and the new polymeric extraction materials [24] have also been recently published. Overall, this review provides a novel, comprehensive and well-discussed overview of the investigation of porous materials as sorbent coatings for use in SPME.

2. Overview of the SPME technique

The introduction of SPME fulfilled the need for a rapid and solvent-free sample preparation technique that facilitated simultaneous pre-concentration and separation of both volatile and non-volatile analytes in complex sample matrices. SPME has been applied for collecting a wide range of analytes from diverse matrix compositions, such as gaseous, liquid, and solid media.

An SPME device is covered with a thin layer of a suitable polymer (liquid, liquid-like, or solid) as a sorbent. The SPME fiber is placed inside the needle of a syringe-like holder. There are two possible configurations of SPME depending on the sample and type of the analytes: direct immersion solid-phase microextraction (DI-SPME) for gaseous and liquid samples, and headspace solid-phase microextraction (HS-SPME) for solid and certain liquid samples (Fig. 2).

Due to the very limited volume of the extraction phase (<1 μL), the extraction efficiency depends on selecting the appropriate coating that ensures a high affinity for the target analytes. From the practical point of view, the selection of SPME fiber coverings is limited to commercially available fibers in various thicknesses and combinations [25]. The choice of the stationary phase is largely determined by the need related to its polarity. SPME coatings can be classified according to three criteria: coating thickness, polarity, and whether the coating is an absorbent or an adsorbent. The available types of commercial fiber are not capable of providing optimal sorption properties for the many different analyte-matrix combinations. Scientists searched for materials with high affinity for the selected analytes and sample matrices. The most popular sorption materials currently available and used so far, used in SPME, are: noble metal nanoparticles [26], silica-based sorbents [27], molecularly imprinted polymers [28], conductive polymers [29], metal [30] and covalent organic frameworks [31] based on carbon sorbents, such as carbon nanotubes [32] and graphene [33]. Most of

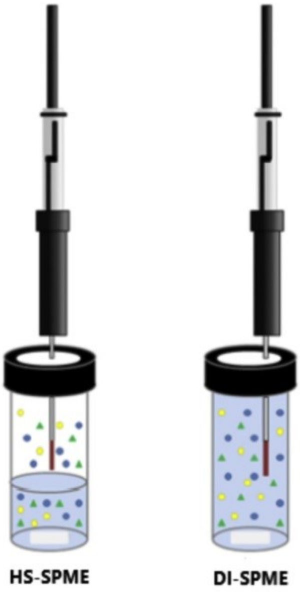
HS-SPME   DI-SPME

Fig. 2. The scheme of the analyte extraction process using HS-SPME and DI-SPME techniques.

overmentioned are adsorptive materials, extract analytes usually by strong interactions of molecules with a solid surface. The adsorbent surface can interact with the analyte by means of π-π interaction, hydrogen bonds, or van der Waals interactions. Considering the way the analytes are immobilized on the adsorbent surface, it is important to consider the thermodynamic basis of the analyte adsorption process.

For a quantitative description of the extraction process, the term “degree of coverage” is used, which can be described by the relationship:

$$\theta = \frac{C^{a}_{ads}}{C_{ads}} \tag{1}$$

where: C^{a}_{ads} - adsorbed analyte concentration based on the volume of the extractant [mol·dm^{-3}]; C_{ads} - total concentration expressed as numbers of active sites based on the volume of the extractant [mol·dm^{-3}];

The above notation of Equation (1) is correct, while assuming that the distribution of active sites on the adsorbent surface is homogeneous. If the Langmuir isotherm model is used to describe the adsorption process of the analyte on the adsorbent surface in the following form:

$$\theta = \frac{K_{ads/p}\, C_{p,eq}}{1 + K_{ads/p}\, C_{p,eq}} \tag{2}$$

where: $K_{ads/p}$ - equilibrium constant of adsorption (partition coefficient), then, after substituting the dependence described by Equation (1) in Equation (2), we obtain a relationship linking the concentration of the analyte on the adsorbent surface as a function of the partition coefficient $K_{ads/p}$ at equilibrium:

$$C^{a}_{ads} = C_{ads}\, \frac{K_{e/p}\, C_{p,eq}}{1 + K_{e/p}\, C_{p,eq}} \tag{3}$$

Based on the analysis of the above equation, it is possible to draw several important conclusions:

- the concentration of the adsorbed analyte is a non-linear function of its concentration in the sample (it has a significant impact on the determination of the calibration curve),
- the linear nature of the relation (3) can be achieved only when the value of the product $K_{e/p} \cdot C_{p,\,eq}$ is much smaller than unity.

However, this only applies when the analyte is present at very low concentration levels or shows little affinity for the adsorbent, (the latter one is rather irrational situation). As a consequence, the process of isolation/enrichment or sampling of analytes is based on the use of adsorption mechanism, which leads to a significant limitation of the linearity range compared to the course of the same process based on the partition mechanism, i.e. absorption. Another important aspect, that may limit the use of adsorbents as stationary phases in the SPME technique is the understanding of the properties of the active surface of the adsorbent described by C_{ads}. This parameter, in equation n (3), characterizes the number of active sites available for one type of analyte. The amount of active sites is constant, however, its availability for a given analyte depends on the affinity of other components of the sample.

In other words, in the case of samples with a complex composition, it is possible for the analytes to compete with other components of the sample for the available active sites on the adsorbent surface. Components with high affinity to the surface of the adsorbent or present in the sample at a high level of concentrations, occupy the available space on the surface of the solid material. As a consequence, this leads to the limitation of both the maximum amount of analytes that can be immobilized on the surface of the adsorbent in the state of equilibrium, as well as the reduction of the linear range of the extraction process [34].

The kinetics of the extraction process in the case of SPME, i.e., a system with cylindrical geometry, is based on the second law of Fick diffusion. However, a simplification involving the omission of the surface curvature is often used. The quantitative description of the extraction kinetics can be described by the following equation:

$$\frac{dn}{dt} = \frac{D_s A}{\delta_S}\left(C_s - C'_s\right) = \frac{D_f A}{\delta_f}\left(C_f - C'_f\right) \tag{4}$$

where: δ_f - the thickness of the fiber coating, δ_s - the diffusion layer thickness in the sample matrix, C'_s – the concentration of the analyte in the sample matrix at the interface of the fiber coating and the sample, C'_f – the concentration of the analyte in the coating at the interface of the fiber coating and the rod, A – the surface area of the fiber coating [35].

The above Equation (4) shows that the speed of the extraction process can be controlled (limited) by diffusion in the double layer (middle term) or the fiber shell (last term). It should be noted that from a practical point of view, the main possibilities of shortening the extraction time relate to the thickness of the double layer, which to some extent can be controlled by selecting an effective mixing method. The remaining parameters in the above equations are practically out of control and are specific to a given fiber-analyte system.

In porous coatings, the diffusion limitation in the fiber coating is relevant only when they constitute the carrier for the actual (liquid) sorbent, which results from the low values of diffusion coefficients in liquids.

In most cases, porous coatings are based on an adsorption mechanism where the pores are filled with a gas phase. Thus, two situations can be considered: extraction directly from the liquid phase and extraction from the gas phase (also headspace). In the first case, due to significant differences in the values of diffusion coefficients (for the gas phase of 10^{-1} cm^2/s, for the liquid phase of 10^{-5} cm^2/s), the mass transport rate is limited by diffusion in the double layer. In the latter case, in practice, the length of the diffusion path inside the pores is generally much shorter than in the gas phase, leading to the conclusion that the process of transporting the analytes to the surface of the fiber shell is the limiting factor. An additional factor that should be taken into account, in this case, is the analyte retention process itself [36]. Unlike the liquid phase, no linear concentration gradient of analytes in the coating can be assumed. The considerations should take into account that due to the relatively short radial diffusion path inside the pores, the analytes very quickly reach their surface, where they are bound. In such a situation, the local concentration of gas-phase analytes inside the pores is lower and equalizes according to the corresponding adsorption isotherm.

Considering the above, it can be assumed that achieving the saturation state in the case of porous coatings based on adsorption is less time-consuming than in the case of liquid coatings.

2.1. *Fiber SPME*

The fiber SPME analysis is typically performed via headspace or direct immersion. In DI-SPME, the high extraction efficiency and adequate sensitivity, the fiber coating for DI-SPME is characterized by compatibility with the sample matrix, robustness, and good affinity toward the analytes of interest. In HS-SPME, the sample is placed in a vial sealed with a cap. The fiber in the HS-SPME mode is placed above the sample in the vial. Therefore, the porous sorbent occupies the headspace of the sample (solid, or liquid) and accumulates the target analytes through the gas phase (semi-volatile and volatile analytes). The HS-SPME mode provides a higher selectivity than that of the direct extraction mode. The clean-up of extracts and a longer fiber lifetime are ensured because the extraction phase is not in direct contact with the sample matrix. The affinity of the extraction phase toward the target analytes is particularly responsible for the extraction efficiency of the HS-SPME technique, making it is suitable for analyzing both volatile and semi-volatile compounds [37].

In both the DI- and HS-SPME modes, porous SPME sorbent coatings can facilitate the selective extraction of all the target analytes in the sample while releasing the other interfering compounds in the matrix. Therefore, porous materials should possess sufficient adsorption capacity to retain all the target analytes. The subsequent elution by an organic solvent or liberation by a temperature increase can easily and completely release the target analytes before their introduction into the detection system. Porous materials with high surface areas are considered to be optimal because of their high sorption capacities. Recently, porous sorbents have been extensively investigated for environmental applications because of their properties such as a high sorption capacity, and in certain cases, high selectivity [38].

2.2. *In-tube SPME*

In 1997, Pawliszyn et al. introduced for the first time the in-tube SPME [39]. In that technique, the extraction phase is coated onto the inner walls of fused-silica tubing. The purpose of the development of the in-tube SPME was associated with its application in high-performance liquid chromatography (HPLC). There are two modes of extraction provided by the in-tube SPME: the draw/eject and the flow-through extraction mode, respectively. In the first mode of extraction, the analyte is extracted through the repeated draw/eject cycles of the sample in the capillary column, until the sorption equilibrium is reached. In the flow-through mode of extraction, the sample is continuously passed through the capillary in one direction. In-tube SPME is described as a highly sensitive and relatively low-cost sample preparation technique, allowing to determine large volumes of aqueous samples, thus enabling the sampling of various polar compounds in biological samples [40,41].

3. Porous frameworks dedicated in SPME

The SPME stationary phases are usually immobilized on geometrically diverse surfaces or packed inside the tubes, needles or syringe tips. The flexibility of device geometry is a domain value of SPME, which allows its multifarious applications; first of all, the coating type of SPME fibers is responsible for the extraction of analytes [42]. The main features characterizing reviewed porous frameworks are given in Table 2.

3.1. *Silica-based coatings*

Silica colloids can be obtained in solution using the Stöber process, named after one of the scientists who first reported such a synthesis [43]. The chemistry of this synthesis is relatively simple and universal at the same time, and so much that it can be used for the preparation of most oxide nanostructures. The synthesis is called the sol-gel process. The sol-gel process is based on the hydrolysis and condensation reactions of suitable metal-organic precursors, such as alkoxides of formula $M(OR)_n$, where M is a metal in the oxidation state *n*, and R stands for the organic group (usually the ethyl and methyl group) [44]. Subsequently, the hydrolysis and condensation reactions lead to the formation of M-O-M bonds, accompanied by the release of water and alcohol molecules, as shown in the following reactions:

Hydrolysis: $(RO)_3Si\text{-}OR + H_2O \text{ -> } (RO)_3Si{-}OH + ROH$

Condensation: $(RO)_3Si{-}OH + RO\text{-}Si(OR)_3 \text{ -> }$
$(RO)_3Si{-}O{-}Si(OR)_3 + ROH$

$(RO)_3Si{-}OH + RO\text{-}Si(OR)_3 \text{ -> } (RO)_3Si{-}O{-}Si(OR)_3 + H_2O$

The procedure appears as a multi-component one and is relatively complicated in selecting suitable synthesis reagents. Sol-gel synthesis is usually performed in a mixture of precursors and pore-former agents, e.g. tetramethylortosilicate (TMOS) [27], and polyethylene oxide [45].

3.2. *Metal-organic frameworks (MOFs)*

The Metal-Organic Frameworks (MOFs) are a newly identified class of porous polymeric materials made of metal ions linked together by organic bridging ligands. The MOFs represent the interdisciplinary development between molecular coordination chemistry and materials science. The novel MOF structures are characterized by the feature amongst the largest pores known for crystalline compounds, very high sorption capacities, and complex sorption behaviour. The establishment of porosity in these polymeric metal-organic structures has been challenging. However, during its development, the main goal opens up the possibilities for

Table 2
Features of the SPME fiber coatings.

Porous framework type	Way of synthesis	Advantages	Disadvantages
Silica-based coating	Sol-gel synthesis	- high extraction efficiency and rate - high porosity allowing for any liquid confinement	- relatively low thermal stability
MOFs	Solvothermal synthesis, solvent-free synthesis, chemical vapor deposition	- either commercially available or easily synthesized; - high acidity (pK_a ~4) allowing for facile *in-situ* deprotonation, - controllable structure composition	- the low conductivity nature and the stability issue; - poor selectivity; - difficulties in regeneration
Carbon-based coatings	Thermal synthesis, chemical vapor deposition	- hydrophobic effect and π-π stacking interaction with the analytes; - high thermal stability of the coating; - applicable for electrochemically enhanced SPME	- low solubility of CNMs in solvents, - relatively low thermal stability
COFs	Solvothermal synthesis, mechanochemical grinding, room temperature synthesis	- the periodic and uniform porosity; - higher internal surface area than their 2D counterparts	- poor hydrolytic and oxidative stabilities

new chemical separations, ion exchange, sensing, and also possibly catalytic behaviour [46]. The MOFs are also described as cost-effective coatings, being developed as an efficient coating material dedicated to the SPME. Since various metal centres and organic linkers are available, MOFs can be synthesized with different structures, topology, and porosity (Fig. 3) [47].

The MOFs as SPME fiber coating was proposed for the first time in 2011. In this work, the ZIF-8-coated fiber was employed to extract and enrich of n-alkanes from biological fluids prior to GC-MS analysis. The recent applications of MOFs as SPME sorbents have been mostly dedicated to complicated biological matrices [30].

3.3. Carbon-based coatings

Since the most often applied carbon-based coatings are those made of multiwalled carbon nanotubes (MWCNTs) and of the graphene-based domain, thus, the attention has been paid to ones in this chapter. MWCNTs consist of multiple carbon nanotubes nested within one another. In each of the MWCNTs, the presence of particular nanotubes can vary even from 3 to over 20, whereas both the internal and external diameter of the nanotubes can vary from 2 nm to over 50 nm. MWCNTs exhibit exceptional electrical, thermal, and mechanical properties. Nevertheless, the increased number of walls provides a higher probability of defects presence than single-walled nanotubes, which results in reduced performances. A significant advantage also is, that outer walls of MWCNTs can be modified with functional groups such as hydroxides, carboxylic acids, or amides, in order to provide the additional functionality (e.g. the ability to attach binding sites for use in biomedical applications [48]). Additionally, MWCNTs are preferred to utilize over the single-walled carbon nanotubes (SWCNTs) as the presence of concentric graphene sheets resulted in an enhanced interaction with the analytes a long MWCNTs (5–15 μm) showed higher sorption capacity than shorter (1–2 μm) MWCNTs. The MWCNTs-SPME fiber is usually fabricated through a dip-coating technique [49].

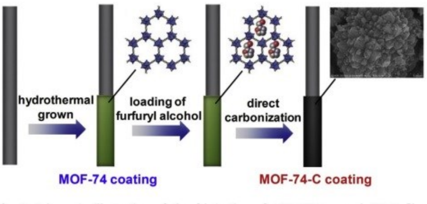

Fig. 3. Schematic illustration of the fabrication of MOF-74-C coated SPME fiber. Copyright 2019 by Elsevier [47].

Graphene is an allotrope of carbon single planar sheet of sp2-bonded carbon atoms that are densely packed in a honeycomb structure [50]. Graphene has been developed as a SPME fiber coating posing remarkable thermal stability, chemical stability and good affinity towards many aromatic compounds. What is more, the extraction performances of SPME fiber coatings could be also improved by the utilization of graphene composites with other materials through covalent modification, non-covalent decoration and doping can also effectively improve. Some of the graphene-based coatings were applied to the SPME technique, e.g. determination of PAHs in cosmetics by a three-dimensional single layer graphitic carbon nitride-modified graphene composite (g-C_3N_4@G) in DI-SPME [51]. Nevertheless, some of the potential applications of graphene as the SPME adsorbent have not been studied yet. Therefore, some of the solutions dedicated to enhancing the graphene-based SPME coating adsorption are provided (e.g., regulation of conformation).

3.4. Covalent organic frameworks

Covalent organic frameworks (COFs) were firstly introduced by Yaghi et al., in 2005 [52]. COFs are characterized by various advantages, such as low density, high porosity, relatively large surface area, crystalline structure, uniform pore size and high thermal and mechanical stability [53]. It has to be emphasized that the synthesis of COFs is made on the basis of dynamic covalent chemistry, what contributes to the formation of its ordered crystalline structure [54]. What is more, COFs can be also designed towards specific purposes, and combined with a wide range of materials [55].

4. Recent applications of porous materials as coatings in SPME

In addition to being reasonable alternatives for commercially available coatings, porous materials prepared using silica, carbon, and MOFs have been extensively applied as coatings, primarily in SPME, and to a lesser extent in other sorbent-based microextraction techniques. The limited number of commercially available SPME fiber coatings necessitates the development of porous sorbents that can provide the desired affinity toward specific analytes; these sorbents can help in extending the scope of applicability of the SPME technique.

A comprehensive review of studies conducted since 2011 on the application of porous sorbents as SPME coatings reveals the increasing levels of interest in newly developed SPME sorption materials (Fig. 4).

New sorption materials are being developed to improve the extraction capacity, sensitivity, and selectivity, and to reduce the matrix effect. However, several modifications have been introduced during the fiber preparation stage and various strategies have been investigated for improving the fiber extraction efficiency of SPME. An ideal SPME sorbent coating should facilitate the separation of all analytes in the solution, and simultaneously release the other compounds of the matrix. Therefore, the SPME sorbent must have sufficient sorption capacity and be able to adsorb all the analytes present in the sample.

In the following section, examples of applications of porous materials mentioned in previous sections are discussed. The essential parameters involved in the SPME process, such as the type of porous sorbent, extracted analytes, sample matrix, extraction and detection techniques, limits of detection (LOD) and quantification, relative standard deviation, linear range instrumentation, and SPME recovery are listed in Table 3.

4.1. Silica-based coatings

Various strategies have been attempted to improve SPME efficiency by taking advantage of the significant role of fiber coatings in the extraction and desorption of analytes in SPME. Liquid (PDMS) and solid coatings (e.g., Carboxen) have been investigated for interacting with analytes through absorption and adsorption mechanisms, respectively [61]. Several SPME stationary phases have been developed to address the difficulties associated with commercial coatings. These include materials produced through sol-gel chemistry [44] (such as ionogels with dip-coating [60,64]) and modification with sputtered silicon [57], aerogels [63], and MIPs [65]. Silica-based SPME fibers have been frequently modified via the addition of ZnO nanorods [58] and magnetic iron oxide nanoparticles [62]. These SPME phases typically possess several advantages over commercially available coatings, such as higher thermal and mechanical stabilities, shorter durations of extraction, higher extraction efficiencies, and longer lifetimes. Nevertheless, some of the newly developed coatings are burdened with certain limitations owing to their complicated synthesis steps. For instance, the preparation involved in the sol-gel approach requires the use of a lengthy procedure to obtain an SPME fiber with a porous structure [96].

The superior extraction capability of sputtered silicon protected by porous PDMS-layer SPME fibers has been reported for the determination of PAHs in tap water via DI-SPME [59]. Extraction efficiencies corresponding to different thicknesses of silicone (0.25, 0.8, and 1.8 μm) and PDMS (8, 16, and 36 nm) were investigated therein. The 1.8-μm-thick silicone coating with 16-nm-thick PDMS produced the optimal response among the tested combinations. The fabricated fiber coatings were characterized by a porous structure and long lifetime and achieved up to 300 analytical cycles. The additional advantage is the lower carry-over between runs and negligible bleeding if compared to commercial coatings.

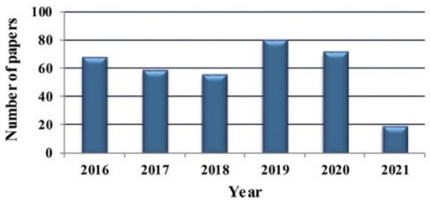

Fig. 4. Recent applications porous sorbents as sorption media in SPME technique, the number of papers with porous sorption media in analytical chemistry (*Scopus database, May 2021; keywords: SPME; silica coatings; carbon coatings; MOF-s, MWCNTs, COFs*).

Several nano-octadecyl silica-based applications in SPME-based methodologies have been recently reported [56,57]. In these studies, the sample flows through a piece of capillary tube that is internally coated with a polymeric sorbent that traps the analytes; this is denoted as in-tube solid-phase microextraction (IT-SPME). For instance, a robust and efficient nano-octadecyl silica (nano-ODS) sorbent coated with spherical silica nanoparticles was designed for the extraction and pre-concentration of ultra-trace levels of PAHs in aqueous samples. The nano-ODS sorbent was prepared using a mixture of tetraethyl orthosilicate (TEOS) with ethanol and ammonia. The results obtained in this study revealed lower LODs and more acceptable recoveries compared to those obtained in other studies [56]. The only exception involved the cold-fiber SPME-GC–MS method [49], which took advantage of the sensitivity enhancement effects of both the cold fiber and MS detector simultaneously. Another nano-ODS fiber coating was proposed by Akbari et al. [57], wherein a vacuum-assisted headspace SPME (VA–HS–SPME) procedure coupled with GC-FID was developed and optimized for the analysis of PAHs in soil. The evaluation of the lifespan and durability of the single fiber was accomplished through more than 150 sampling experiments, with no physical changes observed in the fiber structure and a lack of significant changes in the extraction efficiency (<5%).

The recent development of sol-gel techniques has contributed to the progress in the synthesis of porous materials, especially aerogels. Aerogels are ultralight solids with a density of the order of 1.9–150 mg cm^{-3}. Aerogels are being currently applied in surface modification-based strategies for improving their extraction efficiencies. For instance, ionic liquids (ILs) have been reported to be environmentally friendly extraction solvents [105] and have been therefore considered as replacements for conventional organic solvents. The bonding and hybridization of a bipyridyl IL to a silica aerogel has been reported to improve the mechanical strength and extraction performance of the DI-SPME fiber [63]. Notably, the IL-based silica aerogel exhibited higher LODs than those of the PDMS coatings employed in previously reported analytical solutions. Tian et al. also investigated a hybrid silica aerogel for use in environmental analysis [97]. The results revealed that analyses PAHs corresponded to wide linear ranges, from 0.005 to 20 μg L^{-1}, whereas the remaining analytes were linear in the range of 0.010–20 μg L^{-1}. The extraction performance of the newly developed SPME fiber coating was also compared to that of commercial coatings. The lifetime of the developed fiber, without obvious loss of the extraction efficiency was equal to 120 runs.

The studies described so far were focused on extraction using an adsorption mechanism; however, an absorption mechanism can also be employed using porous coatings. However, in those applications, porous coating serves as a support confining of an actual liquid extractant. Recent attention has been focused on the immobilization of ILs within silica-based porous materials, based on the absorption extraction mechanism [60,64]. SPME fibers obtained using this approach were investigated for the first time with HS-SPME fiber coating prepared using the sol-gel process with potassium silicate as a precursor and dimethylformamide as a pore-forming medium [64]. The immobilization of a 1-ethyl-3-methylimidazolium tetrafluoroborate IL in the silica pores of the

Table 3
Applications of porous sorbent coatings in Solid-phase microextraction techniques.

Type of porous material	Analyte	Sample	Extraction technique	Detection technique	LOD [μg L−1]	LOQ [μg L−1]	RSD [%]	Linear range [μg L−1]	Recovery [%]	Ref.
Silica-based										
nano-octadecyl silica modified fused silica	PAHs	water	In-tube SPME	GC-FID	0.00001–0.00017	N.A.	4.4–10.3	0.00001–0.004	78.7–103.5	[56]
octadecyl silica chemically coated stainless-steel fiber	PAHs	soil	HS-SPME	GC-FID	0.00001–0.00009	N.A.	3.2–10.34	0.00001–0.004	84–111	[57]
fused silica coated by arrayed ZNRs	methanol, n-butanol, dichloromethane, ethyl acetate, acetone	pantoprazole feedstocks	HS-SPME	GC-FID	0.033–0.339	0.10–1.03	6.0–7.1	0.996–0.999	96–107	[58]
sputtered silicon fiber with polydimethylsiloxane (PDMS)	16 PAHs	tap water	DI-SPME	GC-MS	0.6–1.5	N.A.	5–25	1–110	N.A.	[59]
silica-based ionogel: MTMS, TFA with IL, and mixture of two ILs: ([Set3][TFSI]) and ([C4C1Pip][TFSI])	12 VOCs	tap, river and sea water	HS-SPME	GC-BIID	0.07–0.40	0.09–2.27	11.2–30.6	N.A.	88–119	[60]
magnetic iron oxide core-shell silica (Fe_3O_4/SiO_2) nanoparticles	hexanal	urine samples	DI- and HS- SPME	GC-FID	0.00001–0.00005	0.00001–0.0001	5.1–6.6	0.01–10	91–109	[61]
bipyridyl ionic liquid-hybridized silica aerogel	8 PAHs	cigarette smoke and ash	DI-SPME	GC-FID	0.005–0.01	0.015–0.03	1.1–15.6	0.015–20	80.9–119	[62]
organic-inorganic hybrid silica aerogel	8 PAHs	lake and rain water	HS-SPME	GC-FID	0.001–0.030	0.005–0.100	less than 6.1	0.005–20	83.2–118	[63]
potassium silicate and dimethylformamide with IL	12 VOCs	aqueous samples	HS-SPME	GC-BID	0.46–4.23	1.50–12.6	3.2–34.1	N.A.	N.A.	[64]
MCM-41@SiO_2-difenoconazole 3D network	dicofenazole	cucumber, apple and wheat	DI-SPME	GC-ECD	0.00002	0.00005	3.3–9.7	0.0001–0.1	73–103	[65]
Graphene-based										
3D graphene-carbon nanotubes (G-CNTs)	BTEX	lake and river water	HS-SPME	GC-MS	0.00059–0.00268	0.00196–0.00892	3.7–9.1	0.00005–0.5	84.7–108.1	[66]
graphene oxide-based polymer composite coating	5 phenols	Pearl River water	HS-SPME	GC-MS	0.00012–0.00136	0.00038–0.00454	3.1–8.1	0.00005–0.1	81–113	[67]
graphene oxide incorporated polymer monolithic fiber	5 organo-phosphate esters	soil	HS-SPME	GC-FPD	0.00092–0.00072	0.00003–0.00024	5.2–9.0	0.0005–0.01	80.1–105.6	[68]
graphitic carbon nitride	8 PAHs	pond, river, lake, well, rain, snow water	DI-SPME	GC-MS	0.00002–0.00005	0.00007–0.00017	3.1–7.6	0.0007–0.060	83.6–118	[69]
Nanoscale graphitic carbon nitride (nano-g-C_3N_4)Nano-g-C_3N_4/CuO composites	6 PAHs	pond water and soil	DI-SPME	GC-FID	0.00025–0.00040	0.00001–0.00008	2.5–7.3	0.0001–0.01	84.4–108.3	[70]
Molecularly imprinted polymers immobilized on graphene oxide film	triphenyl phosphate	environmental water samples	DI-SPME	GC-FPD	0.00001	0.00004	5.4	0.00007–0.0124	70–110	[71]
sFe_3O_4-g-GO-g-RAFT agent nano-absorbents	4 biogenic amines	smoked fish	DI-SPME	HPLC-UV	0.0009–0.0017	0.00028–0.00049	3.57–5.16	0.0005–0.0150	98.36–103.48	[72]
MWCNTs										
MWCNTs/MnO_2/PEDOT	PAHs	river and lake soil	HS-SPME	GC-FID	0.00001–0.00008	N.A.	2.0–10	0.0005–0.0250	94–108	[73]
MWCNTs/PANI-PPy@PDMS	4 pesticides	garlic	DI-SPME	GC-MS	0.00038–0.00019	1.3–8.3	1.1–11.9	0.001–40	84–108.2	[74]
helical multi-walled carbon nanotube	16 PAHs	Arctic snow samples	DI-SPME	GC-MS	0.00001–0.00012	0.00004–0.00030	1.1–15.0	0.00015–0.030	93.7–119.7	[75]
oxidized multiwalled Carbon nanotubes (CNTs)	7 amphetamine-type stimulants	human urine	DI-SPME	GC-MS	0.2–1.3	0.7–4.3	2.5–5.4	0.5–1000	88–107	[76]
PANI/MWCNT	4 antibiotics; 1 phenol; 3 xenobiotics	milk, lactic acid bacteria beverage, and fruit juice	DI-SPME	MS/MS	0.00015–0.0000.7	0.0005–0.0020	3.2–7.5	5–1000	93.1–102.7	[77]
MWCNTs/PANI/ZIF	4 PAHs	sea, tap and aqueduct water	HS-SPME	GC-FID	0.0003–0.0008	0.9–2.5	0.2–9.7	0.005–1000	83.4–111.2	[78]
MWCNTs and KBF	7 PAHs	river, pond, lake and waste water	DI-SPME	GC-FID	0.04–0.12	50–100	3.5–11.9	0.13–50	80.1–116.3	[79]
MOFs										
metal organic framework (CIM-80 (Al))	13 PAHs	ground coffee, whole milk, red and white wine, apple juice	HS- and DI-SPME	GC-MS	0.0005–0.0015	1.5–5.0	less than 20	0.0005–0.5	99.3–95.3	[80]
metal organic frameworks (MOFs) by direct carbonization	5 odorants	fresh, effluent and tap water	DI-SPME	GC-MS	0.00001–0.997	0.00003–0.3	less than 9.4	0.005–100	83.6–115.5	[47]
nitrogen-doped porous carbon with g-C_3N_4 templated with metal organic framework	14 organophosphorus pesticides	fresh fruit and vegetable	DI-SPME	GC-MS	0.00023–0.00075	0.00069–0.00225	7.8–9.7	0.0069–0.03	82.6–118	[81]
metal organic framework ZIF-8	3 PAHs	wastewater samples	DI-SPME	GC-FID	0.6–2.0	N.A.	5.5–16.0	N.A.	N.A.	[82]

(continued on next page)

Table 3 (*continued*)

Type of porous material	Analyte	Sample	Extraction technique	Detection technique	LOD [μg L−1]	LOQ [μg L−1]	RSD [%]	Linear range [μg L−1]	Recovery [%]	Ref.
MOF with Cu-DAT (copper-2,5-diaminoterephthalate)	10 PAHs	river water	HS-SPME	GC-MS	0.0001 −0.0006	0.00003 −0.00021	4.4 −12.9	0.0001 −0.1	88.4 −105.9	[83]
metal organic framework-monolith composite	5 Fluoro-quinolones	honey and water	in tube-SPME	HPLC-FLD	0.00014 −0.0011	0.00048 −0.0038	less than 10	0.001 −5.0	80.1−120	[84]
COFs										
COFs −TpBD from 1,3,5-triformylphloroglucinol (Tp) and benzidine (BD) with 1,4-dioxane/mesitylene and acetic acid	Bisphenol A	tap, river and sea water	DI-SPME	N.A.	0.00092	0.0031	6.4 −6.7	0.01−10	N.A.	[85]
COFs-TpBD with TEOS and (3-aminopropyl) triethoxysilane (APTES)	16 PAHs	mutton shashlik	DI-SPME	GC-MS/MS	0.00002 −0.00166	0.00007 −0.00552	2.6 −9.4	0.00002 −0.0002	N.A.	[86]
COFs via Shiff base-type linkages (1,3,5-triformylphloroglucinol −paraphenylenediamine)	5 PBDEs	environmental waters	DI-SPME	GC−NCI−MS	0.000058 −0.00022	0.000019 −0.00074	5.62 −9.85	0.00001 −0.00100	71.9 −125.4	[87]
COF − TpPaNO2 ((1,3,5-triformylphloroglucinol and 2-nitro-1,4-phenylenediamine)	11 pesticides	vegetable and fruits	DI-SPME	GC-ECD	0.04−0.25	0.013 −0.083	less than 11.2	0.05 −0.225	81.5−111	[88]
Other sorptive coatings										
triazine-based covalent porous organic polymer	8 PAHs	environmental waters	In-tube SPME	HPLC-DAD	0.004 −0.010	0.013 −0.033	0.3 −3.1	0.0013 −20.0	74−125	[89]
porous membrane soaked in vinyl monomer mixture immobilized with 3-(methacryloyloxy) propyltrimethoxysilane	2,4-dichlorophenoxyacetic acid (2,4-D)	food samples	DI-SPME	MS and Raman spectroscopy	N.A.	N.A.	0.5 −6.0	N.A.	N.A.	[90]
Porous (1-vinyl-3-(4-vinyl-benzyl) imidazolium chloride) IL polymer	6 organic acids	grape wine	HS-SPME	HPLC-CE	0.007 −0.015	0.004 −0.0385	4.84 −15.65	0.01−1.0	78.19 −98.11	[91]
carbon aerogel templated by ionic liquid	6 tetracyclines (TCs)	eggs and poultry farm wastewater samples	DI-SPME	HPLC-UV-Vis	0.36−0.71	1.20 −2.38	1.85 −10.96	2−1000	80.65 −108.68	[92]
carbon aerogel	6 tetracyclines (TCs)	eggs and milk	DI-SPME	HPLC-UV-Vis	0.47−1.05	1.57 −3.49	1.37 −15.81	1−500	82.56 −107	[93]

N.A. −not available.

prepared fiber was studied. The analysis of results based on the enrichment factors (EFs) revealed that the newly developed silica fibers exhibited better performance for extracting volatile organic compounds from water samples, compared to that with the reference PDMS fiber. It is worth emphasizing that silica can be undoubtedly employed as a porous material for the immobilization of ILs because its mechanical stability facilitates the loading of any IL.

The sol-gel methodology enables the production of a hybrid organic/inorganic network in which the IL can be confined [98]. The material obtained in this manner is called an ionogel, which retains the liquid-like nature of the IL. Ionogel-coated SPME fibers based on the solvation properties of ILs have been proposed as HS-SPME fiber coatings [60]. Three compositions of ionogels for SPME fibers were prepared therein using the following ILs as the primary components: triethylsulfonium bis(trifluoromethylsulfonyl)imide, 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide, and their 1:1 M mixture. The EFs of the fabricated fibers were higher than those obtained for the commercial fibers for nearly all the tested analytes. The only exception was *tert*-butylbenzene, for which the PDMS/divinylbenzene (DVB) fiber exhibited the second-highest EF.

The combination of MIPs with microextraction techniques has been recently revealed to be a powerful analytical tool. In most of these studies, analytes were extracted in small and suitable solvent volumes and subsequently diverted for further chromatographic detection-based analysis. Moreover, it should be emphasized that MIPs exhibit high thermal stability (up to 300°C) and are suitable for the SPME-GC technique. In this regard, MIP-based SPME-GC has been applied for the determination of pesticides in fruits and vegetable samples [65] and trimethyl phosphate in environmental waters [99]. The coatings fabricated in these studies represent a strategy involving the formation of a 3D network that was molecularly imprinted on a mesoporous silica-based surface. The results indicated that the fibers demonstrated high selectivity and sensitivity, with an acceptable lifetime.

4.2. Carbon-based coatings

Carbon-based coatings have gained the attention of researchers as alternative sorbents owing to their improved water dispersibility, versatile surface modifications, high mechanical strength, and high surface area. Carbon-based coatings can also be considered as graphite sheets containing a broad range of functional groups, such as ketone and carbonyl groups. Coatings prepared using graphitic carbon nitride (g-C_3N_4) are typically applied as graphene-based fiber coatings for SPME. Several studies have been conducted to determine PAHs using DI-SPME coupled with GC [100]. Zang et al. proposed the modification of g-C_3N_4 with a covalent organic framework (COF-TpBD) [69]. The practical verification of the proposed fiber was investigated using three commercially available fibers. The peak areas of the analytes (PA, PDMS/DVB, and PDMS) were lower than those of the g-C_3N_4@TpBD fiber. The difference possibly resulted from the fact that both g-C_3N_4 and TpBD contained π-conjugated structures, implying that g-C_3N_4@TpBD could effectively adsorb the PAHs through $\pi-\pi$ stacking, and hydrophobic interactions. An analogous situation was reported by Yang et al. [70], in which g-C_3N_4 was modified using a CuO composite via the pioneering facile-chemical-precipitation method (Fig. 5). The comparable LODs and linear range values of both these methods indicate that g−C_3N_4−based SPME fiber coatings possess improved adsorption capabilities compared to those of commercial coatings.

In several studies, graphene oxide (GO)-based coatings have been prepared using the support of added polymer composites in the presence of phenols [67] and organophosphates [68,71] in

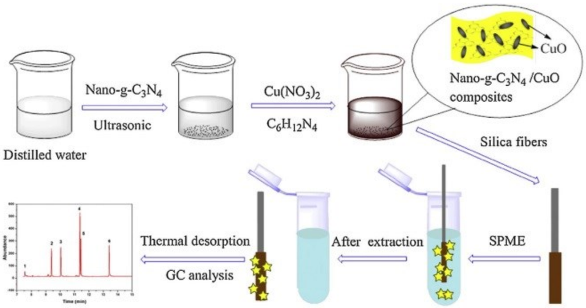

Fig. 5. Schematic demonstration for the synthesis and SPME process of nano-g-C_3N_4/CuO coated fiber [70]. Copyright 2018 by Elsevier.

environmental samples. The GO-based coating modified with highly crosslinked polyoxyethylene improved the thermal stability, water resistance, and biocompatibility of the functional materials. Under the optimized conditions, the extraction of the fiber-coupled with GC-MS detection exhibited low detection limits (0.12–1.36 ng L^{-1}), decent precision (<8.4%), and adequate fiber-to-fiber repeatability (3.1–8.1%). Jian et al. fabricated GO with incorporated poly acrylamide-ethylene glycol dimethacrylate (GO-poly AM-EDGMA), which exhibited the highest extraction efficiency compared to those of two commercial fibers (100 μm PDMS and 80 μm PA). A GO-based coating has also been modified with triphenyl phosphate (TPhP). Interestingly, the purified GO powder was modified with a polymerizable silane coupling agent, 3-methacryloxypropyl trimethoxysilane, which can provide reaction sites for grafting polymers onto it. Under optimal conditions, TPhPMIPs/GO provided a better extraction efficiency for TPhP among those of monolithic graphene fibers and commercial coating fibers. This result was possibly because of the selectivity of the monolithic structure of the TPhPMIPs/GO fiber toward the template molecule and its formation from a significant amount of the nanoscale adsorbents (MIPs/GO). The surface area and pore volume of TPhPMIPs/GO were 669.8 m^2 g^{-1} and 1.399 cm^3 g^{-1}, respectively.

Synthesis methods without the use of catalysts have drawn considerable recent scientific attention. For instance, reversible addition–fragmentation chain transfer (RAFT) polymerization has been proposed as an effective polymerization technique that can be performed under mild conditions without a catalyst. The desired specifications for RAFT can be obtained by the synthetic tailoring of various monomers with predesigned molecular weights or tailing functional groups [101]. Molaei et al. proposed an application of the RAFT polymerization method to develop SPME fiber coatings that can be employed in the extraction and pre-concentration processes of trace-level analysis of organic and inorganic compounds [72]. The novel GO-RAFT approach was attempted in this study for the first time and applied to DI-SPME for investigating the isolation of biogenic amine from smoked fish samples. The desired magnetic nanocomposite was prepared via surface modification of a non-magnetic material derived from Fe_3O_4 nanoparticles. As a result, the saturation magnetization of the sorbent facilitated the facile magnetic separation of the sorbent by utilizing the external magnetic field.

Recent attempts on the development of SPME sorbents have been focusing on three-dimensional (3D) graphene-based nanocomposites produced via the hydrothermal technique. Heydari et al. [102] and Cen et al. [66] fabricated sorbents that were coated on a stainless steel wire using a sol-gel process. Graphene-based materials with 3D structures are characterized by a large inner space, adjustable pore structure, and improved electrical conductivity and mechanical strength. The agglomeration of flexible graphene sheets with a large lateral size is prevented by a partial overlap in the 3D space, which forms an interconnected hierarchical spongy structure [102]. Notably, these fabricated SPME sorbents facilitated comparable or lower LOD values in shorter extraction times compared to those obtained in previously reported analytical solutions. The significant advantage of the 3D graphene-based nanotubes as SPME sorbent coatings was confirmed via real sample analysis of ethion and BTEX in environmental samples.

Me et al. [73] proved the applicability of MWCNTs modified with MnO_2 and poly (3,4-ethylenedioxythiophene) for the selective isolation of target analytes from soil samples. The designed HS-SPME-GC-FID analytical method was noted to provide superior performance with good linearities (0.5–250 ng g^{-1}) and low LODs (0.1–0.8 ng g^{-1}). Hajiazadeh et al. [78] also reported the utilization of the MWCNT–HS–SPME technique for environmental analysis; however, their study involved the use of polyaniline (PANI) and zeolitic imidazolate frameworks (ZIFs) as nanoporous composite coatings fabricated using a layer-by-layer strategy through a decomposition method. The obtained porous structure significantly increased the surface area of the nanocomposite and improved its absorption efficiency toward the target analytes.

Another combination of MWCNT-based DI-SPME sorbent coatings was proposed by Li et al. [77], wherein a knitting benzene monomers with formaldehyde dimethyl acetal (denoted as KBF), and MWCNTs were integrated to form a hybrid material network. The fabricated MWCNT-KBF SPME coating was thermally stable up to ~600°C and exhibited a weight loss of only ~0.81% before 270°C, which suggested that the MWCNT-KBF coating could be applied to the thermal desorption of PAHs via the injection port of the GC-FID system. The extraction performance of the MWCNT-KBF-based SPME was compared to that of other reported methods with different coating materials, such as Ag nanoparticles [103] and C_{18} functionalized GO [104]. The investigated approach was found to exhibit a two-fold improvement in performance in terms of the linear range, LODs, and RSDs compared with those of other relevant SPME methods.

Arcoleo et al. [75] carried out the detection of ultra-trace levels of PAHs in a polar environment. Helical MWCNTs were proposed in this study for the first time as a DI-SPME coating. The MWCNT fiber coatings were obtained by dipping a silica rod into epoxy glue and subsequently in each MWCNT powder, three times. The fiber fabrication methodology was noted to be straightforward, with the possibility of being automated. An additional factor that is also related to the GAC principles involves the low consumption of organic solvents during the fiber synthesis step. Moreover, the utilization of these newly developed fibers combined with the SPME technique has several advantages, such as a short extraction time, high enrichment factor, and ease of operation.

Song et al. investigated the feasibility of using acid-oxidized MWCNTs-COOH as a sorbent coating for HS-SPME to extract amphetamine-type stimulants (ATPs) from human urine [76]. This sorbent was coated on a stainless steel wire via a physical adhesion-based approach, the principle of which was based on the tendency of dissimilar particles to cling to one another (Fig. 6). The physicochemical properties of the MWCNTs were modified by the introduction of oxygen-containing groups onto their surfaces, which facilitated the suitability of the coating for the extraction of ATPs from biological samples. The thermal stability of the MWCNTs-COOH coated fiber was significantly high (300°C at 2 h) and the fiber was used over 150 times.

MWCNT-based sorbents have recently been applied for the isolation of pesticides from food samples. One of these methods involved the application of a thin layer of the PANI nanocomposite on the MWCNT coating through the electrodeposition method [74]. The significant advantage of the newly developed MWCNT/PANI-based SPME fiber was confirmed for extraction purposes. To further explore the extraction potential of the fabricated fiber, certain insecticides were extracted using a commercial PDMS coating. The obtained extraction results indicated that the MWCNT/PANIPPy@PDMS coating exhibited a higher extraction efficiency than that of PDMS toward organochlorine or heterocyclic insecticides. Similarly, Guo et al. investigated the MWCNT/PANI-based SPME performance toward antibiotics and xenobiotics in several food and beverage samples [77]. A streamlined analytical workflow was developed for the analysis of infant drink samples using a miniature MS system that was preceded by SPME and extraction nano-electrospray ionization. The methods described in both these examples have potential for on-site analysis, which has been noted recently to be a trend in modern analytical chemistry.

4.3. Metal-organic frameworks (MOFs)

Among the porous materials that have been explored as coatings, MOFs stand out because of their exceptional surface area, synthetic versatility, easy functionalization, and high thermal stability. The crystalline and highly porous structure of MOFs comprises metal clusters and organic ligands, which help in achieving tunable physicochemical properties; these can facilitate a decent degree of control at the material design stage. An increasing number of MOF-based sorbent coatings have been recently reported; however, only a few studies deal with complex samples using MOF coatings either in HS-SPME or DI-SPME [47,82]. Several combinations of MOF-based materials involve the application of other materials, such as n-doped carbon nanotubes [82] or MOFs obtained via the direct carbonization method [47]. These materials have been typically employed for improving the compatibility between the coating and the matrix.

The evaluation of extraction possibilities was proposed by Pacheco-Fernandez, who utilized a fiber coated with a CIM-80(Al) MOF for the analysis of PAHs in beverage samples via HS- and DI-SPME [80]. The developed fibers were first tested using the HS-SPME-GC-MS method under random preliminary conditions and compared with commercial SPME coatings to evaluate the extraction capacity of the sorbent. The obtained results suggested that this coating could be used for the analysis of water and other aqueous complex samples in the DI mode, without losing its crystalline structure despite lengthy extraction times.

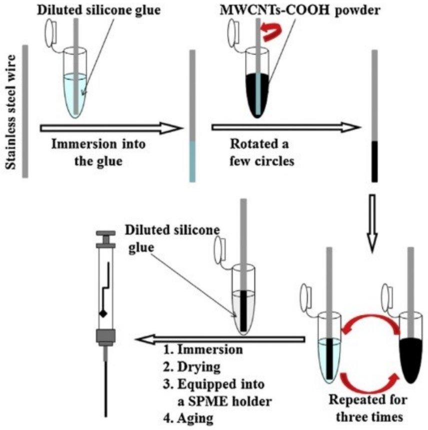

Fig. 6. The fabrication process for MWCT-COOH coated fiber [76]. Copyright 2018 by Elsevier.

A study by Rocio-Bautista et al. involved the production of a MOF ZIF-8 based coating by exposing ZnO layers to a linker vapor (2-methylimidazole) [81]. To obtain a robust MOF-based SPME coating, it is necessary to maintain the adhesion of the crystals to the fiber. The chemical vapor deposition (CVD) method was investigated therein for fabricating MOF thin films. The proposed method was based on a two-step process involving the deposition of the metal precursor layer and its exposure to a sublimed organic linker, which yielded the crystalline and porous MOF films. MOF-based SPME composites were also developed by Pang et al., wherein a ZIF-8 coating was introduced to enhance the surface area of the monolith composite, and to improve the performance of the in-tube SPME of fluoroquinolones from water and honey samples [84]. The RSD values were obtained in the 2.5–9.6% and 0.8–9.8% ranges for water and honey samples, respectively. The validation results provided evidence that the proposed approach showcased high sensitivity and good precision.

A custom-made MOF-based SPME fiber coating was prepared by Qiu et al. through *in situ* heteroepitaxial growth of copper-2,5-diaminoterephthalate (Cu-DAT) for the determination of PAHs in environmental water samples [83]. This study explored an effective and convenient method for preparing highly efficient MOF-based SPME fibers through a dip-coating procedure. The fiber coating was noted to be unstable during the repeated extraction and desorption processes, as the extraction performance for the PAHs decreased to 32.8–48.7% over only five cycles. Compared to the polyimide (PI)–Cu and Cu-DAT fibers, the extraction affinity of the PI(CuDAT) fiber was significantly higher ($P < 0.05$) for all the examined analytes.

4.4. Covalent organic frameworks

Significant recent attention has been focused on porous organic polymers (POPs) with respect to separation and purification technologies. POPs are extensively used in sample preparation because of their superior physical and chemical properties. The advantages of polymers include their rich pore structure, relatively low density, and flexibility in functionalization-based design. Triazine-based covalent organic polymers (COPs) have been proposed [89] as an essential class of POPs, in which the introduction of 1,3,5-triazine rings with aromatic planar π-bonds form a less energetic framework with good chemical stability. Additionally, the presence of nitrogen atoms in triazine-based COPs enables a high binding force with other molecules, which contributes to the improvement in SPME selectivity. In 2021, Yasen et al. [90] reported a novel sandwich method for preparing a robust SPME polymer coating on a glass slide for the first time; a supporting membrane with controllable thickness prepared using polytetrafluoroethylene was also employed. The obtained sorbent exhibited decent mechanical strength and excellent optical properties. The membrane was fabricated via a facile approach to control the thickness of the polymeric composite coating, which yielded a structural frame that facilitated a preparation procedure that could ensure a highly stable coating.

Work proposed by Gao et al., in 2019 [85] was devoted to the synthesis of 1,3,5-triformylphloroglucinol (Tp) and benzidine (BD), via hydrothermal reaction forming TpBD-COF. It was directly adhered to a glass fiber for SPME of tetrabromobisphenol A (TBBPA), to further determine trace TBBPA from water samples. In the case of fragile nature of glass fiber, the physical adhesion method promoted weak coating. The final determination of TBBPA was made by coupling the fiber with constant current desorption ionization MS, towards the determination of trace levels of TBBPA in water samples, providing satisfactory results of LOD and LOQ in the ranges of 0.01−10 mg/L-1 and 0.92−3.1 ng/L-1, respectively. To solve the problem, Ma et al. proposed the chemical bonding of TpDB-COF with polydopamine modified stainless steel wire [86]. In this work, the authors contributed to the chemical bonding of COFs onto the stainless steel wire method development. Also made the possibility of further facilitation of the proposed method in the routine sample preparation laboratory performance.

Another extractive coatings based on COFs were proposed by Liu et al. [87]. The authors have synthesized the ab-ketoenamine-linked COF as the coating of SPME fiber. Advantageously, the excellent specificities such as π-π stacking, hydrophobic affinity, high surface area, and thermal durability, allowed for TpPa-1-COF-coated fiber exhibiting better extraction efficiency than commercial fibers for five polybrominated diphenyl ethers in water samples, accompanying with ultra-low LODs (0.0058−0.022 ng*L^{-1}), with high EFs in the range of 2035−6859. The mechanochemical grinding method was proposed as another simple method was utilized to synthesize Tp-PaNO$_2$-COF [88]. Coupled with GC-ECD, Tp-PaNO$_2$-COF-coated fiber sensitively determined eleven pesticides in vegetable and fruit samples with LODs in 0.04−0.25 mg*kg^{-1}. The mechano-chemical grinding method avoided the complicated preparation process and harsh synthetic conditions, however, it could be only applied to a limited variety of COFs.

4.5. *Other sorptive coatings*

Several studies have recently reported the application of other sorptive SPME coatings.

Several scientific articles are being published recently reporting the preparation and application of other porous SPME coatings. Polymeric ionic liquids (PILs) have also been used as SPME sorbents to extract polar organic acids [90]. The synthesized 1-vinyl-3-(4-vinyl-benzyl)imidazolium chloride IL was subjected to polymerization in the presence of azobisisobutyronitrile and subsequently coated on stainless steel wires for fabrication via physical adhesion. Compared to the direct HPLC/CE method or other previously reported SPME-based techniques, the PIL-based SPME-GC-MS method ensured a long lifetime and decent durability of the fibers. Moreover, these fibers posed a significant advantage in terms of compounds with a large polarity compared to commercial fibers. Another example of the SPME utilization was provided by Souza et al., in 2019 [92]. The authors developed a wall-coated open tubular capillary column with PILs, dedicated for on-line in-tube SPME with UHPLC-MS/MS. The chemically bonded and cross-linked PIL-based sorbent phase (thickness coating: 1.7 nm) presented high chemical and mechanical stability. Utilized in the method PILs enabled the production of selective sorbent phases for in-tube SPME/UHPLC-MS/MS analysis of endocannabinoids (eCBs) in plasma samples from patients with Parkinson's disease. The method presented a wide linear range from 0.1 ng*mL^{-1} to 100 ng*mL^{-1} of determined eCBs.

The evaluation of the robustness of PIL-based coatings was conducted by Gionfriddo et al., in 2018 [93]. In this work, the performances of two PIL-based SPME coatings to assess their applicability for food analysis were examined. Based on the duration of the evaluation of the proposed fibers, the PIL1 coating was estimated as the most robust. What is more, PIL1 has shown a broader extraction capability towards the examined organophosphorus samples compared to 7 μm PA and PDMS coatings. To demonstrate the tunability of the properties of this type of sorbent coating, the authors gave future prospects for a wide range of applications in food analysis.

Other sorptive coatings involve the use of carbon aerogels via DI-SPME for extracting tetracycline antibiotics from food samples [94,95]. A sol-gel-drying-carbonization procedure was implemented with [94] and without an IL [95]. The average pore diameters obtained from the investigation of BET specific surface areas for the IL-based and non-IL-based carbon aerogels were 513.6 m^2 g^{-1} and 416.2 m^2 g^{-1}, respectively. Both structures assisted in increasing the specific surface area and improving the contact between the analyte and adsorbent.

5. Conclusions and future prospects

In recent years, a significant advancement in the SPME technique has been made resulting expansion of its applicability domain. These includes new extracting materials, configurations and calibration approaches to the implementation of state-of-the-art research. Despite the existence of commercially available SPME fibers, the drawbacks associated with their use still exist. The main drawbacks are associated with complex sample analysis, e.g. low affinity towards the polar compounds, and the analytes are retained on the extraction fiber due to specific analyte-adsorbent interactions. Nevertheless, taking into account the research potential of SPME technique in the analysis of real-life samples will definitely direct future research trends toward the design of improved extraction phases capable of overcoming such challenges. Even though the imposing features of the recent SPME coatings involve large surface area, better selectivity, higher adsorption/absorption capacity and pre-concentration factor, and better reusability facilitated the extraction procedure, there is still a great room open to the development of novel solid adsorbents in this area. What is more, the selectivity and productivity of the presented in the review SPME coatings can be enhanced through either different surface modification or combination with other novel substances to produce more efficient porous composites.

The number of new sorption SPME coatings increases significantly year by year, what was recognized as a noteworthy subject enabling new possibilities in sample preparation. The conducted literature review shows that scientific discipline related to new SPME sorption materials is in a continuous phase of development. It is necessary to undertake research aimed at developing new methodological and apparatus solutions in the SPME technique, concerning both the development of completely new design solutions and the modification of the existing ones. Presented in the review solutions concerning new porous materials to SPME have demonstrated a proof of concept. As it was already mentioned, the utilization of commercially available fibers is still restricted. Thus, some expectations covering the development of new commercial coatings based on the presented SPME sorbent coatings does exist. No doubt that SPME with its environmental greenness can replace the conventional extractions in routine laboratory analysis. Direct coupling of SPME with analytical instrumentation is also beneficial, allowing to minimize the analysis time and improving its sensitivity. However, these solutions require providing compatibility with HPLC or GC systems, also taking into account downsizing, allowing portability, and in-field applications.

Despite the advantages of new material solutions in the area of porous materials mentioned in this work, many practical issues require further research. A comprehensive look at the collected publication material shows that most of them describe model tests in conditions that do not fully reflect the problems that can be encountered in the analysis of real samples. This approach is, of course, natural when a new sorption material is presented. Nevertheless, the real verification of the usefulness of new materials is their use in samples with a complex or variable matrix composition. This is a particularly important aspect in porous materials, where we deal with the adsorption mechanism of the isolation of analytes. Therefore, further research should be expected, which will confirm the applicability of newly developed materials in analytical practice in a more unambiguous way (leaving no doubts). Hybrid materials are another direction that has been explored to a very limited extent so far consisted of a combination of solid network and liquid absorbent. Such a material has the potential to combine the advantages of both extraction mechanisms, i.e., the high selectivity of adsorbents with a wide range of absorbent linearity. The introduction of porous materials as SPME sorbent coating allowed the expansion of these materials as extraction phases, e.g., ILs, DES. However, those still require improvement because most of them are utilized in the HS mode. It results from the inability of their use in DI mode (the potential loss of the extraction phase). Thus, the prospects should also be focused on the more effective immobilization of the extraction phases inside the pores of the sorbent, allowing their utilization in DI-SPME, providing to more effective determine less volatile compounds.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Załącznik 3

The new silica-based coated SPME fiber as universal support for the confinement of ionic liquid as an extraction medium

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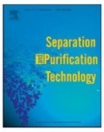

The new silica-based coated SPME fiber as universal support for the confinement of ionic liquid as an extraction medium

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ABSTRACT

The new silica-based SPME fiber coating is reported for the first time as universal support purposed to confinement of ionic liquid as an extraction medium. Fiber coating was prepared by the sol-gel process, using potassium silicate (K_2SiO_3) as a precursor and dimethylformamide (DMF) as a pore-forming medium. The concept of synthesis assumes obtaining a solid porous material on the surface of the glass rod and, being characterized by high porosity, mechanical strength, and uniformity of shape. In the course of the research, several parameters were optimized, like the type of silica precursor, drying steps, time and temperature of aging.

Properties of obtained coatings were evaluated using optical and scanning electron microscopies and thermal adsorption/desorption measurements. Finally, the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate $[C_2C_1IM][BF_4]$ was immobilized in silica pores of the prepared fiber. The usefulness of the obtained SPME silica-IL fibers was investigated by its utilization in model analytical procedures. Robustness of produced fibers is supported by high fiber-to-fiber reproducibility (%) as well as by a long lifetime reaching over 50 extraction/desorption cycles.

1. Introduction

Porous materials, according to IUPAC (International Union of Pure and Applied Chemistry), are defined as solids having pores, channels, cavities or gaps, whose depth is greater than the width [1]. The potential use of porous materials, e.g., zeolites [2], silica gels [3] have found an interest in adsorption [4], catalysis [5,6] and nanotechnology [7], whereas a significant sorption properties are responsible for e.g., liquids and gases separation [8], the removal of soil [9,10] and water impurities [11,12], as well as many other processes. The increased interest of silica materials was also influenced by the fact that these materials show high hydrothermal resistance, whereas the methods of their synthesis are characterized by great universality [13]. Silica is formed from tetrahedral $[SiO_4]^{4-}$ rigid building blocks, however, they can bind through oxygen atoms (forming Si-O-Si bridges), relatively freely, at angles from the linear to the tetrahedral range.

In general, mesoporous silica adsorbents include a wide range of silica-based inorganic porous materials. Despite the mesoporous scale of these materials, the ability to obtain an ordered and homogenous porous structure is relatively better than in the case of other adsorbents [14]. The synthesis of mesoporous silica adsorbents is based on the sol-gel process, which consists of hydrolysis and condensation stages. Hydrolysis is based on a reversible hydrolysis reaction of alkoxy groups of monomer molecules, whenever condensation is strictly related with heterocondensation of alkoxy groups with silanol or homocondensation of silanol groups, derived from silica monomer. The sol-gel process is combined with the templating method, which allows obtaining a material with ordered and regular pore sizes. The aim of that process is to control the interfaces and surfaces of porous materials at the earliest phases of production [15].

In recent years, there is a strong necessity to develop new methodological and technical solutions purposed to sample preparation. One of the most popular sample preparation techniques, which fulfils the requirements of green analytical chemistry, is a solid-phase microextraction technique (SPME) [16]. The performance of SPME, due to the limited volume of the extraction phase (< 1 µL), is critically dependent on the selection of appropriate coating, ensuring a high affinity to target analytes. On the other hand, the choice of commercial coatings

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is not sufficient to cover a variety of analyte-matrix combinations in an optimal way. Thus, for the last two decades, the main direction of SPME development was concerned with novel coating materials, which could be used for the SPME fibers. The highest popularity has gained the following materials: nanoparticles of noble metals [17], sorbents based on silica (silicon dioxide) [18], molecularly imprinted polymers [19], conductive polymers [20], sorbents based on carbon, namely, carbon nanotubes [21] and graphene [22]. Most of the above-mentioned SPME coatings work with adsorption mechanisms (90%), which involves some of the drawbacks, e.g., limited linearity of extraction, the phenomenon of competitive analytes. These limitations do not take place in the "liquid-like" materials, where the analyte isolation occurs with partitioning mechanism (absorption). The material used for this purpose should also meet the following properties: thermal stability in high temperatures, negligible vapour pressure, and existence in a liquid phase in a wide range of temperatures. Substances that fulfil these requirements are ionic liquids (ILs). Ionic liquids may be considered as one of the most flexible groups of chemical compounds in terms of "controlling" their physical and chemical properties by selecting appropriate anion-cation pair. An enormous number of possible combinations of ion pairs, however, have not been disclosed for the sample preparation procedures, yet. It is mainly due to difficulties in the preparation of a stable coating of ionic liquid on the glass fiber. Summarizing, in order to fully explore the potential of ILs as stationary phases in the SPME technique, there is a need to develop the methods of ILs immobilization on a fiber surface in a way that ensures obtaining of mechanically and thermally stable layer.

The investigation of the unique properties of ILs as extraction media in SPME is a widely discussed matter [23]. The first application of ILs in SPME was attempted by Liu et al., in 2005 [24]. Research dedicated to the application of ILs as stationary phases in SPME resulted in the development of several SPME fibers coating preparation methods. Within the application of ILs as sorption materials, the limitations concerning the unstable layer of IL on SPME fiber surface were observed. In order to support the investigation of ILs as extraction phases, a several solutions were proposed. One of the proposed solutions concern the development of polymeric ionic liquids (PILs). PILs are considered as compounds having polymerizable groups in cations or anions, allowing to the formation of polymeric backbone in polymerization reaction [25]. The first use of PILs as SPME coating phases was reported by Anderson and co-workers in 2008 [26]. Another proposed solution concerns the formation of IL-based hybrid materials, on/in which the IL is immobilized [27]. Additionally, in recent years, a new subclass of ILs named magnetic ionic liquids (MILs) has been developed. MILs are fabricated by the inclusion of a paramagnetic component in either the cation or anion of the IL structure [28]. The application of MILs in analytical chemistry have become a key subject in numerous recent reviews [29,30]. Another interesting solutions applying ionic liquids as sorption material is ionogels [31], which consist of a porous silica structure filled by an immobilized ionic liquid (IL). Ionogels are obtained through the sol-gel process, thus, the ILs maintain their original properties inside the porous material [32]. The current application of above mentioned ILs to sample preparation has been addressed by a lot of review articles [16,23,33].

The concept of studies assumes obtaining a solid porous material on the surface of the SPME fiber. The obtained material should have a large pore volume and an appropriate pore diameter that allows for the largest possible loading of the ionic liquid. The aim of this work is to develop and evaluate the methodology of preparation on the glass fiber of the SPME device, of the porous layer acting as support allowing physical confinement of virtually every ionic liquid. However, in the current study as a model IL 1-ethyl-3-methylimidazolium tetrafluoroborate $[C_2C_1IM][BF_4]$ was used. The choice was dictated by its physicochemical properties, like high-temperature resistance indicated by thermal decomposition temperature equal to 350 °C [34], relatively low viscosity, (33.8 cP at room temperature [35]) and relatively low absorption of water [36].

2. Experimental section

2.1. Reagents and materials

The chemicals were used in this study as received and without further purification. Sodium silicate (Na_2SiO_3) was purchased from Merck, whereas potassium silicate (K_2SiO_3) was obtained from Biomus. Chlorotrimethylsilane ($(CH_3)_3SiCl$, TMCS), dimethylformamide (C_3H_7NO, DMF), n-hexane (C_6H_{14}, HPLC grade), methanol (CH_3OH, HPLC grade), silicone oil ($[\text{-Si}(CH_3)_2O\text{–}]_n$) were purchased from Sigma-Aldrich. An ionic liquid, named tetrafluoroborate 1-ethyl-3-methylimidazolium was from Iolitec. The SPME holder for manual sampling and commercial fibers for comparison of polydimethylsiloxane (PDMS, 100 µm) were purchased from Merck (Poland). Before use, commercial fiber was conditioned in the injector for 1 h at 250 °C.

A standard mixture of volatile organic compounds (EPA VOC Mix 2, 2000 µg mL^{-1} in methanol) was purchased from Merck (Milwaukee, WI). The mixture includes following compounds toluene, ethylbenzene, m-xylene, styrene, bromobenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, p-isopropyltoluene, n-butylbenzene, 1,2,4-trichlorobenzene, naphthalene, 1,2,3-trichlorobenzene. Standard working solutions of the VOC Mix 2 were prepared by appropriate stepwise dilution of the stock solution in methanol (HPLC grade was obtained from Merck, Poland) and stored at 4–5 °C.

Aqueous solutions for extraction were prepared by diluting an appropriate amount of sodium sulfate (Merck, Poland) in the ultra-pure water. Ultra-pure water obtained using a Millipore Q system (Millipore, Molsheim, France) was used in all cases. Optical fibers (diameter of glass core is 150 µm) were used to obtain the ionogel SPME fibers. Sulfuric acid, hydrochloric acid, and sodium hydroxide were purchased from POCH (Gliwice, Poland) and used for the pretreatment of glass fibers.

2.2. Instrumentation

Both confined with ionic liquids and non-confined with ionic liquids silica materials have been characterized by Fourier Transform Infrared (FTIR) spectroscopy using the attenuated total reflection (ATR) technique on a Nicolet 8700 spectrometer (Thermo Electron Co.). The Golden Gate ATR accessory (Specac Inc.) was used, equipped with a single reflection diamond crystal. For each spectrum, 64 scans were made with a selected resolution of 4 cm^{-1} within the range of 550–4500 cm^{-1}. A scanning electron microscopy (SEM) was performed on an SEM FEI Quanta FEG (250 in a high vacuum after sputter-coating the samples with a thin layer of gold). Thermogravimetric analysis (TGA) was carried out on a Netzsch TG 209 F3 Tarsus, under air flow, at a temperature range RT - 800 °C with a heating range of 20 °C min^{-1}. Prior to the measurement, the blank run for baseline correction has been performed. A Delta Optical Genetic Pro optical microscope was involved in the performance of images, which were done with the 50 × magnification.

Analyses were carried out on a Shimadzu Tracera system that consists of a Shimadzu GC-2010 Plus GC coupled with a Shimadzu barrier ionization discharge detector (BID-2010 Plus) (Shimadzu Scientific Instruments, Inc., Columbia, MD) and 60 m × 0.32 mm × 180 µm Durabond DB-VRX high-resolution gas chromatography column was used. The carrier gas was helium (99.9999%, Linde Gas, Poland), the injector was operated in the splitless mode, and 220 °C and the detector temperature was 250 °C. The column oven was initially set at 40 °C for 10 min programmed, then increased to 145 °C at 50 °C min^{-1} (for 1 min), then increased to 170 °C at 4 °C min^{-1} (for 1 min), and finally to 225 °C at 10 °C min^{-1}, in which it was held for 2 min.

2.3. Synthesis of porous silica materials and SPME fiber preparation

The first step of the conducted experiments was to examine the properties of porous materials, depending on the selected precursor, respectively, sodium silicate (Na_2SiO_3) and potassium silicate (K_2SiO_3). In all of the performed experiments, as a pore-former agent, dimethylformamide (C_3H_7NO) was used.

The synthesis of silica materials was performed through a single step sol-gel process, as shown in the following reactions:

$$\text{Hydrolysis: } Na_2SiO_3 + H_2O + 2HCl \rightarrow Si(OH)_4 + 2NaCl \quad (1)$$

$$K_2SiO_3 + H_2O + 2HCl \rightarrow Si(OH)_4 + 2KCl \quad (2)$$

$$\text{Condensation: } Si(OH)_4 + (OH)_4Si \rightarrow (OH)_3Si - O - Si(OH)_3 + H_2O \quad (3)$$

Preparation of the glass fiber was aimed at introducing hydroxy groups on the glass surface, that could participate in the reaction with the silica precursor. The expected effect of the modification should be a stronger bonding between the coating and the glass rod, thus, obtaining a fiber with increased mechanical stability. Purposed to surface modification, in performed experiments, the so-called 'acid pyranate' (peroxosulfuric acid, 1:3 (v/v) H_2O_2:H_2SO_4) and NaOH have been used. During the optimization stage, glass fiber was exposed to the reaction mixture for 15, 30, 45, and 60 s. By examining the strength of the coating's bonding to the surface, it was found that while increasing the length of exposure of the fiber increases the adhesion of the coating to the glass surface. However, it was found that too long exposure significantly weakened the fiber glass structure, preventing its practical use. Finally, as the optimal time of surface etching was 30 s. Due to the relatively high viscosity, the starting solution of sodium silicate was pre-diluted with distilled water (v/v, in the ratio of 1:0.5).

The reagents were pre-mixed in an Eppendorf tube, in order to obtain a homogenous solution. After mixing, which lasted 10 min, the resulting solution was injected by the syringe into a tube of a polymer material (PEEK – polyether ether ketone). Firstly, the bottom of the PEEK tube was closed by GC septum to prevent leakage of the sol solution, while previously prepared glass fiber was placed inside the tube in such a way, that it was possible to close also the top of the tube. The whole system was placed in a closed Eppendorf tube (to avoid the evaporation) as it is shown in Fig. 1. After gelation, fiber was retracted from the PEEK tube and subjected to subsequent stages of procedure, as shown in Fig. 2.

2.4. Confinement of ionic liquid

In the last step, the process of confinement of ionic liquid inside the pores of silica material was optimized and evaluated. The process was performed in the round bottom glass flask, suitable for low-pressure working conditions. Prepared fibers were immersed in the ionic liquid and placed in the flask filled with silica oil, ensuring thermal contact with the heating chamber, as shown in Fig. 3. The applied procedure consists of two steps: in the first, using a vacuum pump, the air was removed from pores of the coating; in the second step, elevated pressure pressed ionic liquid into void volumes. The first step was terminated based on the visual inspection when no air bubbles can be noticed on the surface of the fiber (ca. 120 min). The vacuum was obtained using the pump, for which the maximum under-pressure was equal to $2 * 10^{-2}$ mbar. After that, the pressure was slowly increased up to the atmospheric one in which fibers were kept for a given time. The process of inclusion into the pores strongly depends on the of IL's viscosity. Despite the fact that viscosity of the liquids decreases with the increase of the temperature, to facilitate the transfer of ionic liquid through the pores, the higher possible temperature was applied. The temperature was limited by the boiling point of silicone oil under the applied vacuum and equals ca. 150 °C; thus, in the experiments, the temperature of 120 °C was accepted as a safe one. Under those conditions, the time required for complete filling of pores was determined based on TGA analysis of fibers exposed in IL's from 1 up to 10 h. Results have shown that the amount of accumulated IL's stopped growing above 6 h of exposition, thus that time was used for IL's confinement.

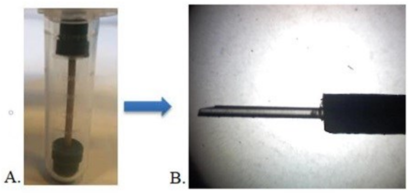

Fig. 1. A. Both sides sealed the PEEK tube placed in an Eppendorf tube. B. Photography of the exemplary fiber retracted from PEEK tube after gelation.

2.5. Mercury injection capillary pressure (MICP)

The MICP method is a well-established and useful technique, dedicated to characterization of diverse types of porous media, because it provides a wide range of information, e.g. effective porosity, pore size distribution, specific surface area of a sample [37]. Studies of the pore space with the investigation of the MICP method were performed with the use of the Micromeritics AutoPore IV 9520 mercury porosimeter. The sample before analysis was dried at 105 °C for at least 24 h to remove moisture from the pore spaces and then cooled to room temperature (~23 °C) (API-RP 40/98, ASTM-D4404-10, 2010). The analysis was carried out assuming the sample evacuation to 50 µm Hg (6,67 Pa) for 2 min and the equilibrium time of 10 s. Pressure was measured at 102 points in the range of 0.5–60,000 psi (0,003 MPa – 413,7 MPa).

2.6. N_2 Gas adsorption

The pore size distribution determination was performed based on BJH adsorption isotherms of liquid nitrogen at the temperature of 77 K. Prior to N_2 measurements the samples were dried at 150 °C for 6 h under helium flow, and then at 110 °C under vacuum for 8 h, up to the final pressure of 0.001 Torr.

2.7. Analytical procedure

Obtained porous silica fibers were installed on a commercial SPME device (Supelco, Bellefonte, PA). The extraction of VOCs from a standard aqueous solution was performed with headspace solid-phase microextraction (HS-SPME). All the extractions were carried out in a 15 mL glass vial sealed with a screw cap with Teflon-faced septum. Prior to the extraction, the 12 mL of 20% sodium sulfate (w/w) standard solution was exposed to the thermostat for 20 min at 45 °C. Then, 10 µL of 100 µg mL^{-1} VOC Mix 2 stock solution was added to the salt solution and stirred at 1800 rpm for 10 min. After obtaining a homogeneous solution, the SPME was carried out in headspace mode at 45 °C for 30 min. After extraction, the fiber was immediately injected into the port of the GC injector for thermal desorption at 220 °C for 10 min, which proved to be sufficient to ensure complete desorption with no carryover.

3. Results and discussion

3.1. Optimization of composition of sol solution

Four solutions were prepared for both types of water glass (both Na_2SiO_3 and K_2SiO_3), using different volume ratios of DMF to water

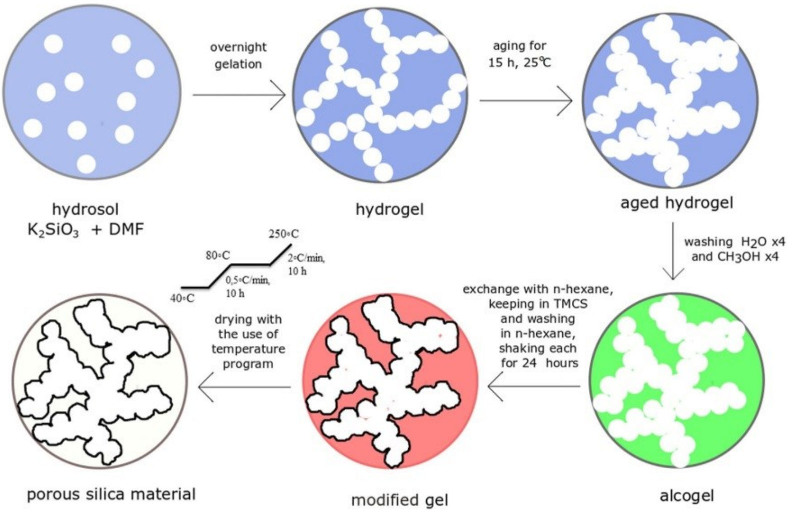

Fig. 2. Flow chart of the experimental procedure for the synthesis of the porous silica material.

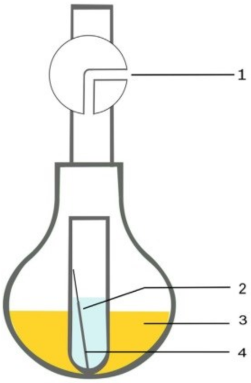

Fig. 3. Scheme of the ionic liquid immobilization process inside the pores of the silica material, where: 1- vacuum, 2 – ionic liquid, 3 – silicone oil, 4 – SPME fiber.

glass of 1:5, 1:10, 1:15, and 1:20. Reactions were carried out in Eppendorf tubes in that the appropriate amounts of DMF were added dropwise to the water glass solution, followed by mixing until both components were completely mixed. After the closing of Eppendorf tubes, the solution thus obtained was stored at room temperature for a period of 15 h. The obtained gel was subsequently aged for 24 h at room temperature.

SEM images of obtained porous silica materials are shown in Fig. 4. The general observation, as can be seen, is that the average pore size for the potassium precursor is, for each dilution, smaller than for the sodium precursor. Considering that the immobilization of the ionic liquid in the pores is based on the action of capillary forces, too large pore diameter seems an undesirable property. At the same time, it was found that the presence of large pores in silica obtained from the sodium silicate resulted in increased fragility of the material, which in later studies could change into shortening the time of application of the fibers. Based on the results, only the potassium silicate precursor was used in further studies.

The practical use of SPME fiber coatings is determined by their several properties. The most relevant are those related to physical evaluation, i.e., the regularity of the coating, its thickness, and mechanical strength. We expected that the well-known phenomenon of shrinkage of the silica gel during post-treatment stages like aging and dying would play a critical role in the coating preparation. Taking into account uniform chemical bonding of the coating to the glass fiber and unfavorable geometry of the coating i.e. length/thickness ratio, the next steps of optimization were performed using target glass fibers. The thickness and regularity of the coatings were evaluated with the use of optical microscopy.

In the next stage, the ratio of K_2SiO_3 precursor to DMF was evaluated, which was carried out by visual examination and mechanical strength assessment of the fibers. Fig. 5 shows images from an optical microscope based on which this assessment was made. Analyzing, the most promising fibers are those made in a 1:5 and 1:10 IL/DMF volume ratio, they are similar to each other. Fibers made from sol solutions with a ratio of 1:15 and 1:20 were rejected due to visible cracks in the coating structures. Finally, the thickness of the two best fibers was assessed. The assessment was based on images from an optical microscope as shown in Fig. 5. A greater value of fiber thickness was obtained using a sol solution with IL/DMF ratio of 1:5, thus that sol composition was used for further research.

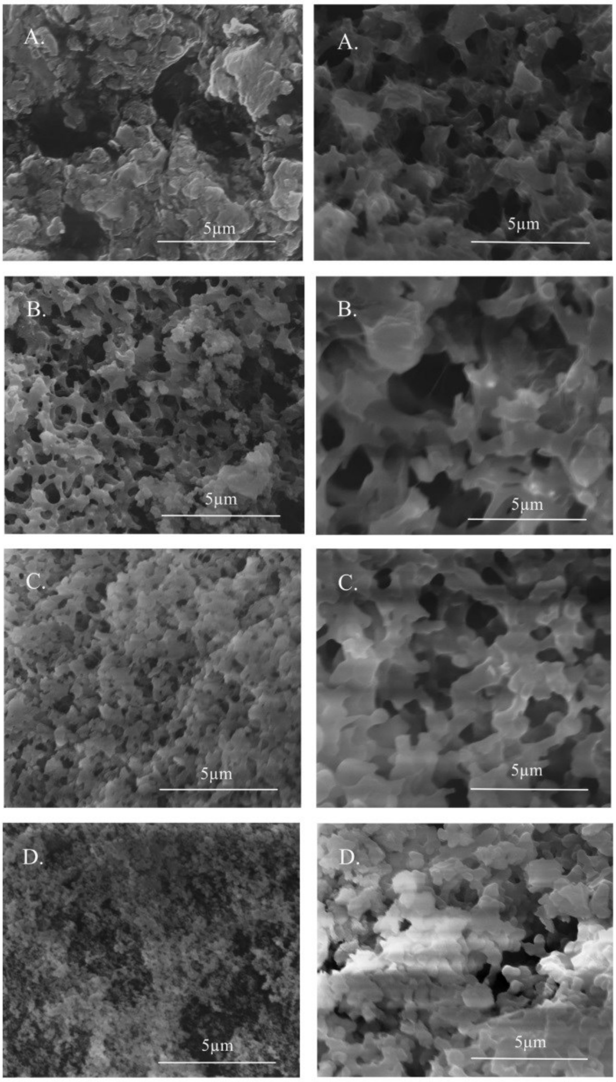

Fig. 4. SEM micrographs of silica porous fibers, where A – 1:20, B – 1:15, C – 1:10 and D – 1:5, of DMF to precursor, respectively. On the left column of K_2SiO_3 precursor, on the right column Na_2SiO_3.

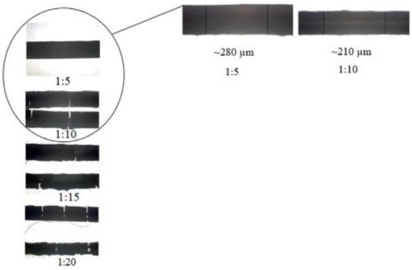

Fig. 5. Images of coatings made of water glass and DMF, deposited on glass fiber, taken with an optical microscope.

3.2. Post-treatment procedures

The thickness and regularity of the coatings were evaluated with the use of optical microscopy. In Fig. 5, sample images of prepared porous silica fiber coatings are shown. It could be observed that all of the presented coatings have a rather flat surface with small roughness areas. The visible differences in the thickness of the coatings appeared with the utilization of the different precursors during the synthesis.

The last stage, which was optimized, was the aging process, where the optimized parameters were temperature and time. The tests used temperatures 25, 60, and 80 °C for 4, 8, 12 and 24 h (Fig. 6). In that step, the parameters of cracking and regularity of the coating were taken into consideration. Based on the pictures taken with an optical microscope, it appears, that both of these requirements were met by the fiber aged at the temperature of 25° C. The cracks occurring for the fiber aged at 60 °C and fiber irregularity occurring at 80 °C of aging were the factors contributing to the failure to meet the abovementioned conditions of the coating.

The final evaluation of the fibers was carried out after their thermal treatment consisting of heating at 250 °C for 1 h. The obtained results of the visual evaluation of the coatings are presented in Table 1. Based on the performed evaluation, the most suitable fiber selected was the one aged at 25 °C for 24 h.

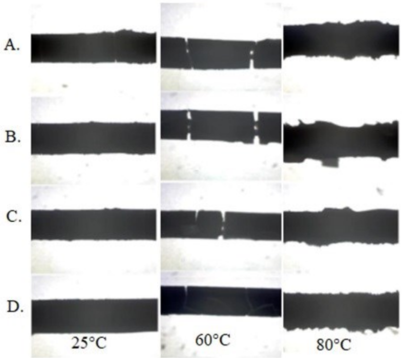

Fig. 6. Pictures of fibers after aging at different temperatures, where A. 4, B. 8, C. 12, and D. 24 h of aging.

Table 1
Summary of the relationship between time and temperature at which the fibers were aged. The table evaluates the fibers obtained, where "−" means severe cracking of the coating, "+/−" - single cracks, "+" - no cracks.

		Temperature (°C)		
		25	60	80
Time (h)	4	–	–	–
	8	–	–	–
	12	+/−	–	–
	24	+ (selected)	+/−	–

Finally, fibers were coated with the synthesized material, an ionic liquid was confined inside its pores, and then, installed on a compatible SPME device. The procedure of preparation of the porous silica matrix originated from several performed so far studies concerning the synthesis of porous silica materials. In the vast majority of the procedures, the sol-gel process is involved. Briefly, the silica precursor is mixed with a pore-formed in the presence of a catalyst. Firstly, the mixture gains the structure of the sol (solid particles as a colloidal suspension), then it turns into the structure of the gel. The whole reaction is supported by two parallel reactions, i.e., hydrolysis and condensation.

3.3. Evaluation of obtained IL- silica fibers

3.3.1. FTIR spectroscopy

The functional groups of the $[C_2C_1IM][BF_4]$ ionic liquid (IL), silica material (silica fiber), and silica material with immobilized IL (silica-IL fiber) were investigated by FTIR analysis and the spectra are shown in Fig. 7. The spectra corresponding to the silica material reveal the nature of the functional groups present in it. The intense and broadband appearing on the silica fiber spectrum at the about 1090 cm^{-1} wavelength and the shoulder of about 1200 cm^{-1} in silica material (red and blue lines) corresponds to asymmetric stretching vibrations Si–O–Si in the transversal optical and longitudinal optical modes, respectively. On the spectra also observed the symmetric stretching vibrations of Si–O–Si at around 793 cm^{-1} and the wavelength of 960 cm^{-1} appear the Si–O in-plane stretching vibrations of the Si–OH groups [38].

The intense and broad peak appearing in the 1030–1060 cm^{-1} range in IL spectra is assigned to the vibration of BF_4 groups. However, due to the overlapping bands of the IL and silica-IL spectra in the range of 1000–1100 cm^{-1}, it becomes impossible to estimate the content

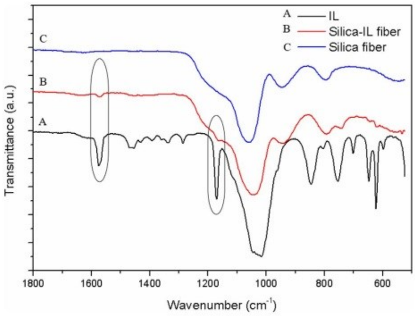

Fig. 7. FTIR spectra of ionic liquid and silica matrix with and without ionic liquid. Ovals indicate peaks of the IR spectra indicating the presence of IL in the silica coating.

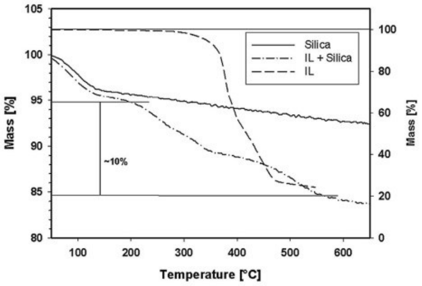

Fig. 8. TGA of pure $[C_2C_1IM][BF_4]$ (dashed line), pure silica material (solid line), and IL + Silica hybrid material (dash-dot line). Y axis: left referred to silica and hybrid materials, right referred to pure IL measurements.

ionic liquid in the silica pores. However, in the IL and silica-IL spectra is appearing peak at the wavelength of about 1565 cm^{-1}, which is not observed on the silica spectrum. This peak corresponds to the appearance of imidazole functional groups in the material. Some other peaks appearing in the IL's spectra, i.e., weak peaks appearing in the 1130–1150 cm^{-1} and 730–745 cm^{-1} range is assigned to the functional groups containing F – atom(s), and weak peaks in the 600–1400 cm^{-1} range is assigned to the C–C and C–N functional groups, however, last two, due to low intensity cannot be used for IL's identification.

3.3.2. TG analysis

TGA analysis was performed for porous silica material, containing ionic liquid and without it (Fig. 8), under the following conditions: heating up to 800 °C (20 °C min^{-1}), in ambient air atmosphere. The results of the thermogravimetric analysis for both materials indicated the decrease of mass by 4% from 140 °C. The possible reason for this decrease is water content, which after the stage of modification of the surface of the porous material was adsorbed from the environment. Between 200 °C and 550 °C, second, a two-step mass drop can be observed. There is a small change in the mass drop rate around 350 °C. However, a similar phenomenon might be noticed in the coarse of decomposition of pure ionic liquid (with a borderline around 400 °C). Thus, the mass loss in the temperature range from 200 °C up to 550 °C equal 10% was assumed to be a consequence of the decomposition of confined IL. Taking into account the mass of the sample used for TGA measurements (1.05 mg) and density of the $[C_2C_1IM][BF_4]$ (1.294 g cm^{-3} [24]) the estimated volume of IL confined in the pores of silica coating was equal 0.08 µL.

3.4. Mercury injection capillary pressure (MICP) and N_2 gas adsorption

The material of the coating was characterized by two techniques mercury intrusion porosimetry and nitrogen adsorption (Tables S1 and S2). The results of both measurements are shown in Fig. 9. Both techniques were used ranges of measurable pore diameters. Based on the collected data one might notice that obtained porous material contains, virtually, only pores with diameters in the range from 0.15 up to 0.45 µm, with an average at 0.32 (standard deviation of fitted Gaussian peak σ = 0.060 µm) (Table 2). N_2 adsorption measurements indicated the presence of pores with an average diameter of 24 Å, however, their total volume is negligible. The obtained pore size range in the range of ± 3 σ can be considered satisfactory for the synthesis method used.

3.5. Utilization of the obtained fiber for the extraction of VOCs

In the final stage of evaluation of a new route of preparation of ionic liquid confined SPME fiber coatings, prepared fibers were utilized in model extractions. The extraction of a set of volatile analyses of different polarities was performed from the headspace of water samples. As our goal was to verify usability of prepared fibers, no to look for optimal extraction conditions, experiments were performed under typical conditions, settled based on available literature: desorption time 10 min, desorption temperature 220 °C, extraction time 30 min, extraction temperature 45 °C, salt concentration 25% (Na_2SO_4), sample volume 12 mL, analytes concentration in range from 5 up to 100 ppm [39]. As a reference, commercial fiber with 100 µm thick, PDMS coating was used. Comparison of extraction abilities of manufactured

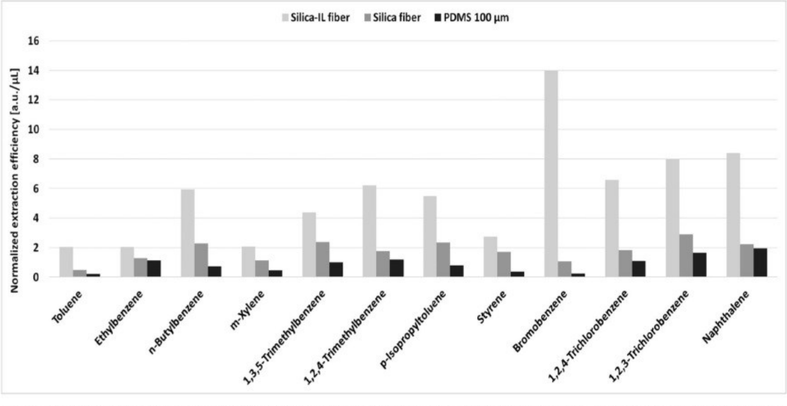

Fig. 9. Comparison of silica fibers with, without ionic liquid and with PDMS fiber in extracting VOCs at concentration 83 µg mL^{-1}. Experimental conditions: sample volume, 12 mL; Na_2SO_4 concentration, 20%; extraction temperature, 45 °C; equilibration time, 10 min; stirring speed, 1800 rpm; extraction time, 30 min; desorption temperature, 220 °C; desorption time, 10 min.

Table 2
Characteristic of fibers used in the study.

Length of coating [mm]	Glass rod diameter [µm]	Coating thickness [µm]	Average pore diameter [µm]	Standard deviation of pore diameter [µm]	Porosity of fiber coating [%]
11	150	65 ± 5.7	0.33	0.061	57.3

Table 3
Analytical characteristics of the developed HS-SPME-GC-BID method for VOCs determination using investigated silica-IL fiber, and extraction efficiency of silica, silica-IL, and PDMS fibers.

Compound	EF			Silica-IL fiber			
	Silica fiber	Silica-IL fiber	PDMS	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)	Repeatability of single fiber (RSD %, n = 5)	Repeatability of fiber-to-fiber (RSD %, n = 3)
Toluene	1030	4360	390	4.23	12.68	10.9	34.1
Ethylbenzene	3240	8700	3760	1.59	4.78	8.5	23.2
m-Xylene	2550	6430	1190	1.81	5.44	7.4	15.9
Styrene	4750	8180	1150	1.55	4.66	7.9	15.9
Bromobenzene	4520	35,190	840	1.62	4.86	5.4	14.9
1,3,5-Trimethylbenzene	5740	12,800	2950	0.82	2.46	3.7	5.7
1,2,4-Trimethylbenzene	4390	16,350	3760	0.77	2.32	6.6	19.2
p-Isopropyltoluene	5970	16,150	2360	0.74	2.21	3.7	7.0
n-Butylbenzene	5860	18,180	2270	0.65	1.96	12.6	29.4
1,2,4-Trichlorobenzene	8720	34,420	6570	0.59	1.78	5.1	9.4
Naphthalene	7800	32,630	8870	0.46	1.39	3.6	10.9
1,2,3-Trichlorobenzene	13,970	42,100	10,220	0.50	1.50	3.2	8.0

fibers and a commercial one was performed using areas of chromatographic peaks determined for investigated analytes. Considering the differences in the diameter and length of the coatings, the areas were normalized by dividing them by the volume of coatings of the examined fibers. As can be seen in Fig. 9, the sum of peak areas for silica fiber with confined IL in pores structure is significantly higher for all analytes than the respective values obtained using silica fiber without ionic liquid. The sum of peak areas of the increased from 41% for styrene to 86% for bromobenzene, due to the immobilization of the ionic liquid in silica pores. The above observation confirms the significant absorption potential of ionic liquid as extractant as well as a dominant role of IL in the extraction process.

The enrichment factors (EFs) were chosen as a reliable parameter for evaluating the extraction abilities of the investigated sorbents. The EF was calculated as the ratio of the analyte concentration in the fiber to the analyte concentration in the water sample. The EFs values of silica, silica-IL, and PDMS fibers summarized in Table 3. The results in Table 3 showed that fibers based on silica material exhibited better performance for the extraction of volatile organic compounds from the water samples, compared with the PDMS fiber.

The limits of detection (LOD) estimated for the HS-SPME-GC-BID method for 12 of VOCs by using silica-IL fiber were based on the lowest detectable peak (defined as signal/noise = 3). The obtained values of LODs lies in the range from 0.46% for Naphthalene up to 4.23% for Toluene. The LOQs were calculated in the same way as LODs only based on a signal-to-noise ratio of 9 and were found in the range from 1.39 to 12.68%. Additionally, the repeatabilities of single fiber and fiber-to-fiber were evaluated by five and three replicate analyses, respectively. The value of the repeatability of single fiber identifies the method repeatability and varies between 3.2 and 12.6%. In turn, the average repeatability of silica-IL fiber is consists of 16.1% and does not exceed the value of 34.1%. The obtained values are included in Table 3. Remarkably, a single ionogel fiber could be used with no obvious decline of performance for about 50 extraction/desorption cycles. After 50 cycles, the EFs start to be systematically below the established average value from previous experiments; thus, we assumed that 50 extraction/desorption cycles are the admissible lifetime of the fiber.

4. Conclusions

In this work, the new silica-based SPME fiber coating was developed as universal support for the confinement of ionic liquid as an extraction medium. Obtained silica fibers were purposed to the confinement of ionic liquid inside the pores of the synthesized matrix. In that case, the conditions in the context of the appropriate precursor, components of the reaction mixture, aging process and fiber conditioning have been optimized. In the silica network obtained by the sol-gel reaction of the K_2SiO_3 precursor and DMF as a pore-former (1:5 v/v), an ionic liquid $[C_2C_1IM][BF_4]$ was confined. Obtained silica fibers allowed to their evaluation by the extraction of volatile organic compounds from the headspace of an aqueous solution. The presented silica-based system allowed the performance of many cycles of extractions for about 50 extraction/desorption cycles. Enrichment factors calculated for investigated samples were in the ranges from 1030 to 13,970 for silica fiber, 4360–42,100 for silica-IL-fiber and 390–10,200 for PDMS fibers. Obtained such relatively high values exhibits evidence for the extraction abilities of selected ionic liquid as an extractant in separation techniques. It indicates that a progressive path for the selection of relevant ionic liquids to be used as extraction phases of different types of analytes is declared.

CRediT authorship contribution statement

Karolina Konieczna: Conceptualization, Data curation, Formal analysis, Investigation, Funding acquisition, Methodology, Visualization, Writing & original draft, Writing - review & editing. **Kateryna Yavir:** Data curation, Methodology, Software, Validation. **Mansoure Kermani:** Investigation, Methodology. **Aleksadra Mielewczyk-Gryń:** Visualisation, Resources. **Adam Kloskowski:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to

influence the work reported in this paper.

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Appendix A. Supplementary data

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Supplementary Materials

The new silica-based coated SPME fiber as universal support for the confinement of ionic liquid as an extraction medium

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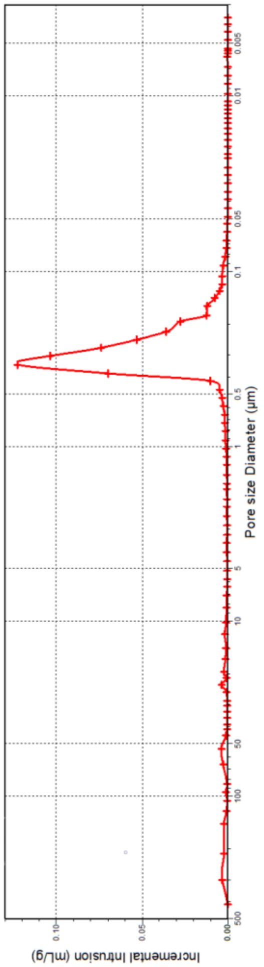

Figure S1. Mercury Intrusion Porosimetry: Plot of incremental intrusion vs pore size. The measurement was performed with the use of AutoPore IV 9500 V1.09 Micrometrics Instrument Corporation.

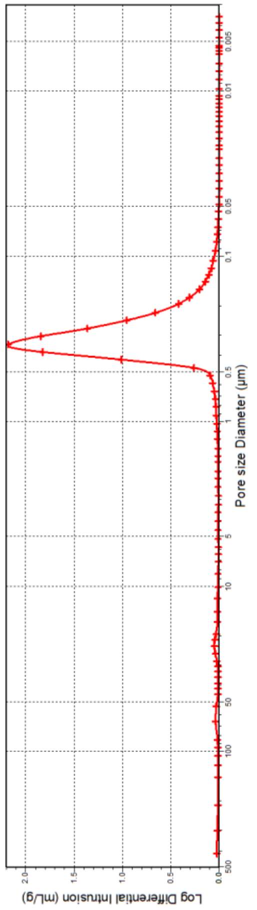

Figure S2. Mercury Intrusion Porosimetry: Log differential intrusion vs. Pore size diameter. The measurement was performed with the use of AutoPore IV 9500 V1.09 Micrometrics Instrument Corporation.

Table S1. Mercury Intrusion Data Summary.

Total Intrusion Volume =	0.6100	mL/g
Total Pore Area =	8.234	m^2/g
Median Pore Diameter (Volume) =	0.3291	µm
Median Pore Diameter (Area) =	0.2887	µm
Average Pore Diameter (4V/A) =	0.2964	µm
Bulk Density at 0.51 psia =	0.9405	g/mL
Apparent (skeletal) Density =	2.2064	g/mL
Porosity =	57.3726	%
Stem Volume Used =	60	%

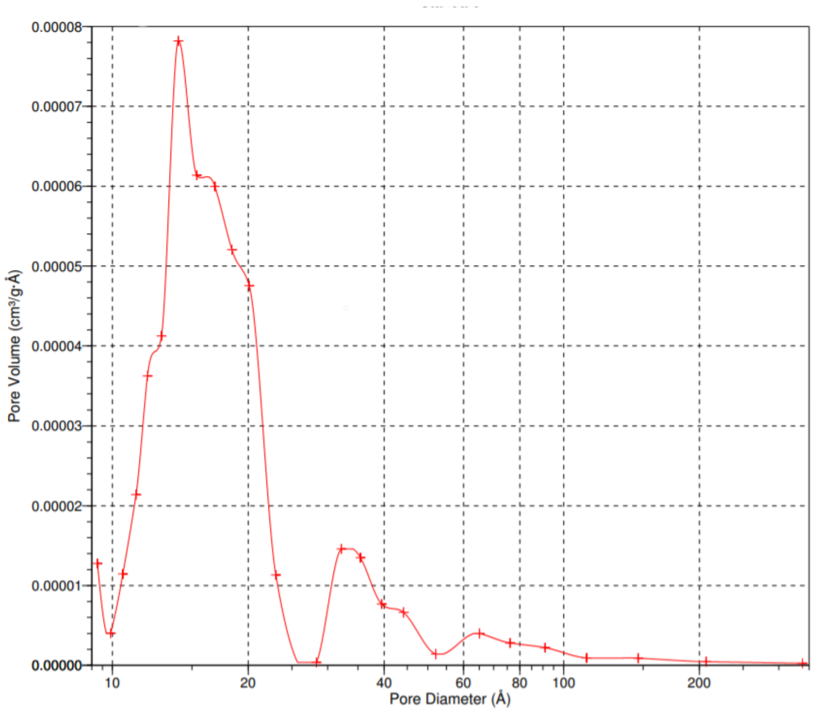

Figure S3. N_2 adsorption results: BJH adsorption dV/dD pore volume. The measurement was performed with the use of Physical sorption analyzer ASAP 2010, Micromeritics Instrument Corp.

Table S2. The data of N_2 adsorption analysis.

Surface Area	Single point surface area at P/Po = 0.243519980: 0.8525 m^2/g BET Surface Area: 1.0627 m^2/g
BJH Adsorption cumulative surface area of pores	between 1.000 Å and 3000.000 Å diameter: 1.847 m^2/g
Pore Volume	BJH Adsorption cumulative volume of pores between 1.000 Å and 3000.000 Å diameter: 0.001136 cm^3/g
Pore Size	BJH Adsorption average pore diameter (4V/A): 24.592 Å

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Załącznik 4

Development of SPME fiber coatings with tunable porosity for physical confinement of ionic liquids as an extraction media

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Development of SPME fiber coatings with tunable porosity for physical confinement of ionic liquids as an extraction media

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ABSTRACT

Extending the use of ionic liquids in sample preparation techniques remains a challenge. This paper presents procedures enabling the easy application of ionic liquids to the SPME technique. For this purpose, two approaches for producing a porous silica coating on a metal rod were investigated. Two silica precursor and porogen systems were used in the research: K_2SiO_3 + Formamide and Tetramethyl-orthosilicate + Polyethylene oxide. The procedure was optimized concerning its operational parameters: the possibility of immobilization of a possibly large volume of ionic liquid and mechanical strength and thermal resistance. In the course of the research, it was shown that the optimal parameters are ensured by using K_2SiO_3 with Formamide. The obtained material had an average pore diameter equal to 0.326 µm with a surface area of the pores similar to 6.33 m^2/g. The size of the pores allows for the quantitative introduction of the ionic liquid and its immobilization to the extent of enabling the extraction of VOC and their subsequent thermal desorption. Finally, the conducted experiments showed that the dominant mechanism of retaining analytes in the IL-silica hybrid material is their dissolution in the ionic liquid, while adsorption on the silica surface plays a lesser role.

1. Introduction

Determination of analytes present at trace levels in samples with complex matrix composition (e.g., biological or environmental samples, etc.) is often an integral part of environmental assessment and monitoring and scientific research in the field of analytics of environmental pollutants. Due to the low levels of analyte, it is necessary to perform a preliminary step of analyte enrichment or isolation before the final analysis. Nevertheless, a limited number of analytical techniques are sensitive enough for the direct determination of trace components and are currently present in laboratory routines. One of the most popular solvent-free sample preparation techniques is the Solid Phase Microextraction technique (SPME) [1–3].

The extraction of analytes with the SPME technique is performed by direct exposure of a fibres covered with a sorption material in an analyzed sample or its headspace. SPME is widely applied in analytical practice because of its undoubted advantages, but one of its limitations is the small choice of commercially available stationary phases and fibres coatings. Due to the limited volume of the extraction phase (<1 µL), SPME performance is critically dependent on the selection of appropriate coating, ensuring a high affinity to target analytes. A properly selected stationary phase enables the extraction of a variety of analytes with enhanced selectivity. Currently, there are polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacrylate (PA), Carboxen (CAR), and polyethylene glycol (PEG, Carbowax, CW), available in various thicknesses and combinations of commercial SPME fibre coatings [4–5]. Most of them operate based on the adsorption mechanism, which exhibits some important drawbacks, i.e., the competitive adsorption of residual components in complex samples, narrowing of the linearity of the extraction process, and possible degradation of entrapped analytes in the course of their thermal liberation in the injector unit of GC instrument. These limitations can be eliminated to some degree by applying an extraction medium in a liquid or “pseudo-liquid” state.

One of the most promising groups of compounds that could be applied as absorbents in SPME are ionic liquids (ILs) [6–8]. ILs fulfil all fundamental requirements like high thermal stability, they are in a liquid state in a wide range of temperatures, and finally, they possess negligible vapor pressure. The main limitation for the applicability of these materials is related to the low durability of the obtained layer of ionic liquid on the SPME fibre surface.

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To overcome those problems, in this work, we propose creating a porous solid network on the surface of an SPME fibre. The porous material will support nano-confinement in its pores of any desired ionic liquid. This way, ionic liquids entrapped by capillary forces will be immobilized on the SPME fibre surface in the form of a stable layer. The versatility of the proposed matrix will be related to the immobilization of the various types of ionic liquids (of different polarities). The most important advantage of this solution is the opening of the opportunity to perform in the future a systematic study on the extraction properties of ionic liquids in connection to their chemical structure.

Since porous materials are defined as solids having pores, channels, or gaps, whose depth is greater than the width (according to IUPAC (International Union of Pure and Applied Chemistry), [9] their utilization is opened to a wide spectrum of possibilities. The application of porous materials, e.g., zeolites [10], silica gels [11], have found an interest in adsorption [12], catalysis [13–14], and nanotechnology [15], whereas sorption properties are responsible for, e.g., liquids and gases separation [16], soil [17–18], and water decontamination [19–20]. Since silica are comprised of rigid, tetrahedral [SiO_4] building blocks, they can bind through oxygen atoms (forming Si-O-Si bridges) with great universality [21]. Therefore, the investigation of silica materials has been of long-standing interest, especially through sol–gel technology. Examples of sol–gel produced fibre coatings exist for a variety of substrates, such as carbon nanotubes (CNTs) [22], ceramic/carbon composite [23], and low-temperature glassy carbon [24]. These studies have proven that sol–gel technology and immobilized resin are suitable coating methods dedicated to solid sorbents.

The proposed work aims to develop and evaluate the methodology of silica preparation on the surface of metal core fibres of an SPME device to provide a porous support allowing physical confinement of ionic liquids. Ionic liquids may be considered one of the most flexible chemical compounds in terms of "controlling" their physical and chemical properties by selecting an appropriate anion-cation pair. However, an enormous number of possible combinations of ion pairs have not been applied in the SPME context yet. This is mainly due to difficulties in preparing a stable coating of ionic liquid on the fibre's core of SPME devices.

Our research so far concerned the preparation of ionogel coatings using silica precursor and ionic liquid combined in a single solution. However, the obtained coatings were characterized by a relatively low content of ionic liquid (0.08 μL). In this work, the production process of ionogels was modified and consisted of two separate stages: creating a porous silica coating and subsequently introducing ionic liquids into its void. Two silica precursors: K_2SiO_3 and tetramethyl-orthosilicate (TMOS); and two porogenic compounds: Formamide (FA) and Polyethylene-oxide (PEO) were tested in the research. The preparation of porous silica has been optimized in terms of pore diameter and volume to ensure high loading of the coating with ionic liquid while maintaining mechanical strength. Additionally, to increase the time (cycles) of using the fibers, the coating synthesis procedure was adapted to the metal core of the SPME fiber made of stainless steel. Finally, the utility of the obtained fibers was verified practically by carrying out the extraction of volatile organic analytes from the headspace of water samples.

2. Experimental

2.1. Reagents and materials

The chemicals were used in this study as received and without further purification. Potassium silicate (K_2SiO_3) was obtained from Biomus. Chlorotrimethylsilane (($(CH_3)_3SiCl$, TMCS), formamide (CH_3NO), polyethylene oxide (PEO, 20 kDa), tetramethyl orthosilicate (TMOS), acetic acid (CH_3COOH, 0.01 M), hydrofluoric acid (HF (40%)), chloroauric acid ($HAuCl_4$ (2%)), n-hexane (C_6H_{14}, HPLC grade), methanol (CH_3OH, HPLC grade), ammonia water (NH_4OH (0.01 M)), and silicone oil ($[\text{-Si}(CH_3)_2O\text{-}]_n$) were purchased from Sigma-Aldrich. Stainless steel (metal core) wires were purchased from Sadevinox, France. An ionic liquid, named 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was obtained from Iolitec.

A standard mixture of volatile organic compounds (EPA VOC Mix 1, 2000 μg mL^{-1} in methanol) was purchased from Merck (Milwaukee, WI). The mixture includes following compounds: chlorobenzene, p-xylene, o-xylene, cumene, n-propylbenzene, 2-chlorotoluene, 4-chlorotoluene, *tert*-butylbenzene, *sec*-butylbenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene. Standard working solutions of the VOC Mix 1 were prepared by appropriate stepwise dilution of the stock solution in methanol (HPLC grade was obtained from Merck, Poland) and stored at 4–5 °C.

Aqueous solutions for extraction were prepared by diluting an appropriate amount of sodium sulfate (Merck, Poland) in the ultra-pure water. Ultra-pure water obtained using a Millipore Q system (Millipore, Molsheim, France) was used in all cases. A stainless steel fibers (diameter of metal core is 150 μm) were used to obtain the ionogel SPME fibers.

2.2. Instrumentation

The base silica formed on wires and combinations with ionic liquids were characterized by Fourier Transform Infrared (FTIR) spectroscopy using the attenuated total reflection (ATR) technique on a Nicolet 8700 spectrometer (Thermo Electron Co.). The Golden Gate ATR accessory (Specac Inc.) was used, equipped with a single reflection diamond crystal. For each spectrum, 64 scans were collected with a selected resolution of 4 cm^{-1} within the range of 550–4500 cm^{-1}.

Scanning electron microscopy (SEM) was performed on an SEM FEI Quanta FEG 250 (in a high vacuum after sputter-coating the samples with a thin layer of gold). Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer TGA 8000, under argon flow, at a temperature range of RT - 1000 °C with a heating rate of 20 °C min^{-1}. Prior to the measurement, a blank run for baseline correction has been performed. A Delta Optical Genetic Pro optical microscope was involved in the collection of images at 50 times magnification.

Studies of the pore structure were investigated with the Mercury Injection Capillary Pressure (MICP) method on a Micromeritics AutoPore IV 9520 mercury porosimeter. Samples were crushed prior to analysis dried at 105 °C for at least 24 h to remove moisture from the pore spaces and then allowed to cool to room temperature in a desiccator (~23 °C) (API-RP 40/98, ASTM-D4404-10, 2010). The analysis was carried out with samples kept in a vacuum at 50 μm Hg for 2 min. The equilibrium time was 10 s. Pressure was measured at 82 points in the range of 0.5–60 000 psi.

Analyses were carried out on a Shimadzu Tracera system that consists of a Shimadzu GC-2010 Plus coupled with a Shimadzu barrier ionization discharge detector (BID-2010 Plus) (Shimadzu Scientific Instruments, Inc., Columbia, MD) and 60 m × 0.32 mm × 180 μm Durabond DB-VRX high-resolution gas chromatography column was used. The carrier gas was helium (99.9999 %, Linde Gas, Poland), the injector was operated in the splitless mode, and 220 °C and the detector temperature was 250 °C. The column oven was initially set at 40 °C for 10 min programmed, then increased to 145 °C at 50 °C min^{-1} (for 1 min), then increased to 170 °C at 4 °C min^{-1} (for 1 min), and finally to 225 °C at 10 °C min^{-1}, in which it was held for 2 min.

2.3. Synthesis of porous silica materials

The first step of the conducted experiments was to examine the properties of porous materials, depending on the selected precursor, respectively, potassium silicate (K_2SiO_3) and tetramethyl orthosilicate (TMOS). In the performed experiments either formamide (CH_3NO) (FA) or polyethylene oxide (20 kDa) were used as a pore-former agent. The selection of the indicated precursors and pore-formers was dictated by procedures from a literature review [25–27].

The synthesis of silica materials was performed through a single step sol–gel process, as shown in the reactions in the Fig. 1.

The reagents were pre-mixed in an Eppendorf tube, in order to obtain a homogenous solution. After mixing, the solution was left to allow gelation. Due to the two methodologies of the porous silica material preparation, the individual steps of the both syntheses are shown separately in Fig. 2 and Fig. 3.

The samples were prepared using several reagent ratios and concentrations of CH_3COOH (TMOS and CH_3COOH ratios were constant). Acetic acid acts as a catalyst. Corresponding variants of the synthesized samples are shown in the Table S1. The analysis concerned also the materials synthesized for PEO (10 kDa) and (35 kDa) and TMOS.

The first stage of the silica material synthesis consisted of dissolving PEO (20 kDa) in acetic acid. This stage lasted about 10 min. The temperature of the PEO solution (20 kDa) with acetic acid was lowered to 0 °C until a homogeneous mixture was obtained. Then, after reaching 0 °C TMOS was added to the solution. This operation was necessary due to the lengthy process of dissolving TMOS. At the lowered temperature, the hydrolysis of TMOS is practically stopped, which allows for better control of the kinetics of the reaction system. Finally, each of the solutions was mixed until the system was homogeneous (approx. 1 h).

According to the diagram presented in Fig. 3, the next step in obtaining porous material was gelling of the solutions, which was achieved by increasing the temperature to 50 °C. The gelation process was carried out in closed glass vessels in which the materials were placed for 24 h. After the gelation stage, the material samples were visually assessed, characterizing the gel's colour, transparency, and hardness (mechanical strength).

At this stage of the research, it was impossible to predict which of the obtained structures is more favourable for the final stage of immobilization of ionic liquids. Therefore, it was decided to produce ionogels using both types of materials. In the final stage, all samples were washed with methanol and left to dry in open vessels at 50 °C for 2 days. Finally, further evaluation of the obtained silica materials was carried out utilizing SEM analysis and mercury porosimetry.

Synthesis of the porous material in the second system (Fig. 3) were made in the 1:2; 1: 5; and 1:10 vol ratios (porogen: precursor, respectively). The reactions were carried out in Eppendorf tubes, so that appropriate amounts of FA were added dropwise to the water–glass solution and then stirred until both components were thoroughly mixed. The solution thus obtained was stored at room temperature for 24 h. The resulting gel was purified by washing (while shaking) with methanol, water, and n-hexane. The last stage was the drying of the obtained porous material at 40° C for 48 h.

2.4. SPME fibres preparation

A stainless-steel wire was washed with methanol to remove organic pollutants and then rinsed with ultrapure water. Subsequently, the cleaned stainless-steel wire (15 mm long) was etched in 40% hydrofluoric acid for 5 min at 40 °C. Afterwards, the etched stainless-steel wire was washed with ultrapure water and dipped into $HAuCl_4$ of 2% (w/w) for chemical deposition of an Au layer onto the surface of the etched stainless steel wire for 30 min at 30 °C. Next, the produced fibres were rinsed with ultrapure water and dried in the air. Then, the Au-coated fibres were dipped into an ethanolic solution of 3-mercaptopropyl triethoxysilane, 1 mM, for 60 min at room temperature. Excess solution was removed. In the next step, the fibres were washed with ethanol and ultrapure water, and then, the fabricated fibres were dipped into the silica-based coating mixture. The mixture was prepared according to the procedure outlined in section 2.3. The silica gel solution was inserted into a non-reactive polymer material (PEEK-polyether ether ketone) with a syringe. The bottom of the PEEK tube was closed by GC septum to prevent leakage of the sol solution, while a previously prepared stainless steel fibres were placed inside the tube so that it was possible to close the top of the tube. The whole system was placed in a closed Eppendorf tube (to avoid the evaporation) as it is shown in Fig. S1. Finally, the fabricated fibres were conditioned in the SPME-GC interface until the stable line was achieved.

2.5. Confinement of ionic liquids

The process of immobilization of an ionic liquid in the pores of the silica material was carried out based on dip-coating technique. The procedure was carried out in the round bottom glass flask, suitable for low-pressure working conditions. A porous material to be filled was immersed in the ionic liquid and placed in the flask filled with silica oil. The purpose of the latter one was to ensure thermal contact with the heating chamber. The procedure relied on two steps: First, vacuum was applied to remove air from the pores of the coating; second, at elevated pressure ionic liquids was pressed into void volumes. The selected ionic liquid was 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide. The selection of the model ionic liquid was followed by its physicochemical properties, like high-temperature resistance indicated by thermal decomposition temperature equal to 381 °C [28] and

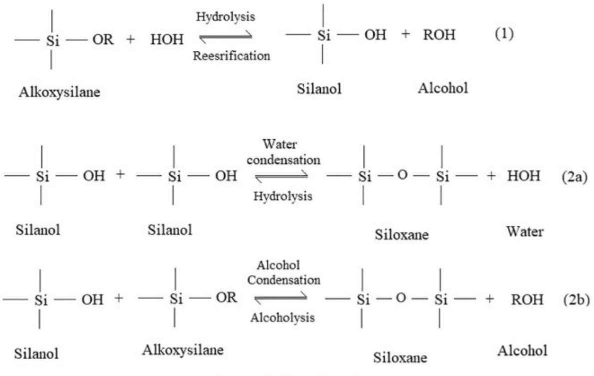

Fig. 1. Sol-gel reaction scheme.

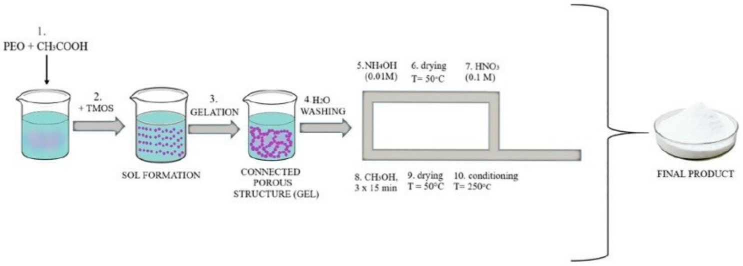

Fig. 2. Sol-gel synthesis procedures using TMOS as precursor and PEO as a pore-forming substance.

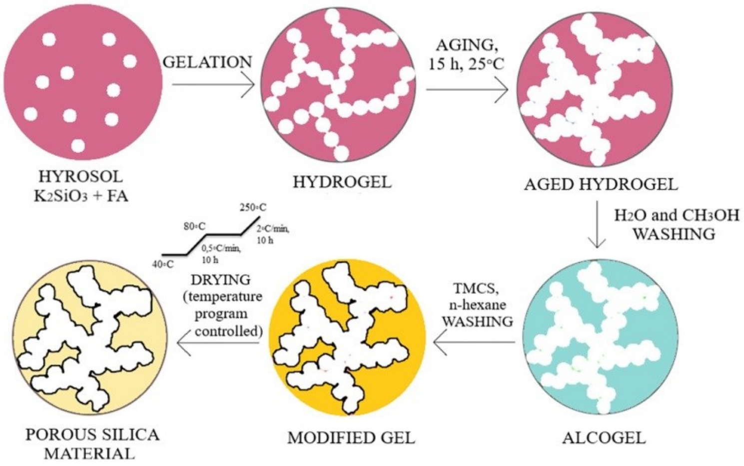

Fig. 3. Flow chart of the experimental procedure for the synthesis of the porous silica material with the utilization of K_2SiO_3 and FA.

moderate viscosity (153 cP) [29].

The first step was evaluated by visual observation; no air bubbles could be noticed on the surface of both fibres and the porous material (ca. 30 min). The vacuum was obtained using a pump at a maximum under-pressure equal to $3*10^{-3}$ mbar. Then, the pressure was slowly increased up to the atmospheric one at which fibres were kept for a given time. To facilitate the transfer of ionic liquid through the pores elevated temperature was applied. The temperature was limited by the boiling point of silicone oil under the applied vacuum and equals ca. 150 °C; thus, in the experiments, a temperature of 120 °C was accepted as a safe one. Under those conditions, the time required for complete filling of pores was determined based on TGA analysis of fibres exposed to IL's from 0.5 up to 5 h. The amount of accumulated IL's stopped growing after 2 h of exposition, thus that time was used for IL's confinement.

3. Results and discussion

3.1. Evaluation of the obtained materials

Seven solutions were prepared for TMOS and PEO, using different concentrations and volume ratios (see Table S1) of PEO. Based on the obtained SEM images (Fig. 4), it was found that a targeted porosity could be obtained using PEO (20 kDa) and TMOS. Reactions were carried out in Eppendorf tubes. After the closing of Eppendorf tubes, the solution was stored at room temperature for a period of 15 h. The obtained gel was subsequently aged for 24 h at room temperature.

The gel in samples no. 2 showed the highest hardness, but the gels present in samples 3 and 4 were relatively easy to crumble. Each of the obtained samples was divided into two parts - one part of the material was subjected to all the steps of synthesis indicated in Fig. 2, and the other half - excluding steps 5–7 (namely, addition of 0.01 M NH_4OH, drying in T = 50 °C, and addition of 0.1 M HNO_3). The omission of steps 5–7 was intended to determine the effect of those steps on the final pore size distribution. It is worth noting that the use of macromolecular

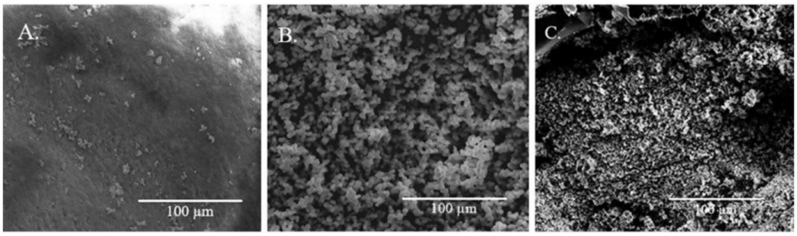

Fig. 4. SEM images of porous materials synthesized using TMOS and PEO with different molar masses: A. 10, B. 20, and C. 35 kDa.

compounds (in the described PEO studies) aims to create macropores with diameters of the order of micrometers. In fact, the etching process in step 5 creates ideal conditions for the formation of meso- and micropores. In terms of mechanical strength, sample no. 2, (with etching) showed the best properties, although it was better if etching steps were omitted. The best properties were shown by the samples without the etching process.

SEM images of obtained porous silica materials are shown in Figure S2 (see Supplementary Materials). The general observation is that the average pore size for the second variant of the solution prepared (Table S1) is the most preferable. Considering that the immobilization of the ionic liquid in the pores is based on the action of capillary forces, too large a pore diameter seems undesirable. At the same time, it was found that the presence of large pores in other variants of the prepared silica solutions resulted in increased fragility of the material, which could shorten the lifetime of the fibres.

The practical use of SPME fibres coatings is specified by several properties. The most essential are those related to physical evaluation, i. e., the regularity of the coating, its thickness, and mechanical strength. An expected issue concerns the phenomenon of shrinkage of the silica gel during post-treatment procedures, e.g., aging, which would play a critical role in the coating preparation.

The ratios of TMOS precursor to PEO were also evaluated by mechanical strength assessment of the material, with the most promising samples being number 2 and 5. However, the latter displayed an undesirable (too large) porosity. The other variants were rejected due to the powderous nature of the materials. The rejected materials could be easily crushed by hand. The most suitable sample, No. 2, for further research was chosen.

Similarly, the materials made from K_2SiO_3 and FA were analyzed. The variants of K_2SiO_3 and FA solution at ratios of 1:2; 1:5; 1:10 (v/v) were analyzed by SEM (Fig. S3). On the basis of the assessment of the porosity of the material in the indicated variants, the ratio of 1:5 was selected for the further research.

3.2. *Mercury injection capillary pressure (MICP)*

The porous material obtained from K_2SiO_3 and FA and for the second system (PEO and TMOS were analysed by mercury porosimetry, confirming the presence of the porous structure of the obtained materials (Table 1, Figures S4 and S5).

Table 1
Characterization of the obtained porous materials by mercury porosimetry.

Material evaluated	Median pore diameter (volume) [μm]	Median pore diameter (area) [μm]	Average pore diameter [μm]	Total pore area [m²/g]	Total porosity [%]
K_2SiO_3 + FA	0.262	0.188	0.326	6.33	50.35
PEO + TMOS	0.202	0.119	0.128	27.44	52.11

The obtained data, i.e., pictures and the results of the mercury porosimetry analysis (Figures S2, S3, and S4), confirmed the presence of channels and interpenetrating voids and the silica skeleton. In principle, it was concluded that the pores could facilitate the penetration of ionic liquids at the stage of their implementation. Both materials (K_2SiO_3 + FA and PEO + TMOS were compared in terms of porosity (Table 1.). The parameters obtained from the MICP method for the studied materials indicate a homogeneous pore structure. The porosity is similar for all samples and amounts to slightly more than 50% of the total sample volume. The highest mercury intrusion is observed for the pore diameters smaller than about 0.3 μm, corresponding to the macropores realm.

The shape of the intrusion curve for the K_2SiO_3 + FA sample indicates the uni-modal character of the pore space dominated by macropores in the range from 0.3 μm to 0.08 μm (Figure S4). The value of the average pore diameter for the K_2SiO_3 + FA is 0.326 μm (Table 1). In the PEO + TMOS sample the intrusion curve indicates a right-skewed distribution of the pore space, shifted towards mesopores (Figure S4). The average pore diameter for the PEO + TMOS sample is 0.128 μm (Table 1).

The pore area is a property that, together with the porosity and the pore diameter, characterizes the connectivity of the pore space. The surface area of the analyzed materials is differentiated and amounts to 6.33 m^2/g (K_2SiO_3 + FA) and 27.44 m^2/g (PEO + TMOS), respectively (Table 1). For the distributions of surface area with respect to pore sizes, the MICP results are presented in Figure S5. It clearly shows, that there is an inverse relationship between pore size and surface area, and the smaller the pore diameter, the steeper the curve of pore area. Thus, pore surface area is predominantly controlled by pores < 0.3 μm.

The materials differ significantly in structure but have similar porosity; differences in pores sizes are essential for the brittleness of the material. Taking into account the parameters characterizing silica materials utilizing mercury porosimetry, it can be seen that the average pore diameter of K_2SiO_3 + FA is three times higher than of the TMOS and PEO. However, in the case of a silica material made of TMOS and PEG, it does not meet the mechanical expectations.

3.3. *Thermogravimetric analysis*

Thermogravimetric analysis (TGA) was performed for one indicated porous silica material with and without ionic liquid (IL) confined inside its pores (Figure S6.). The results of the TGA for both materials indicated a decrease of mass by 5% from 105 °C. The possible reason for this decrease is water content, which was adsorbed from the environment during sample preparation. Between 220 °C and 530 °C, a second two-step mass drop can be observed for the sample containing IL. There is a small change in the mass drop rate around 420 °C. However, a similar phenomenon might be noticed in the course of decomposition of pure ionic liquid which can be seen in the Figure S7 (with a borderline around 400 °C). Thus, the mass loss (about 55%) in the temperature range from 220 °C up to 530 °C was assumed as a consequence of the decomposition of confined IL.

For comparison, silica material directly scraped from the fibres were also analysed by TGA. The results of the analysis were included in Supplementary Materials (Figure S8).

3.4. *Fibres coating evaluation*

The last step is to check the material in practice, by its application in a real analytical procedure. The characteristics of the prepared fibres and the silica coating deposited on the metal core is shown in Figure S9. An ionic liquid was immobilized inside the pores of the fibre according to the previous procedure. The process of inclusion into the pores is strongly dependent on the of IL's viscosity. The viscosity of ionic liquids decreases with an increase in temperature.

The analysis of the obtained SPME fibres was carried out using an optical microscope. The fibres have the following dimensions: Diameter of the metal core: 150 µm, diameter of fibre coverage with silica: 306.88 µm. The obtained fibres were of a regular thickness, without noticeable cracks. The pore diameter for an individual fiber was determined based on 11 measurements along with the fiber (every 1 mm, total length 10 mm); at the same time, the repeatability of the fiber-to-fiber preparation was determined based on the measurement of 5 fibers; in the first case, the irregularity of the coating did not exceed 5% (307 ± 15); and the fiber-to-fiber (322 ± 29).

The selected ionic liquid was immobilized in the obtained porous silica coating and verified by TGA under similar conditions as the K_2SiO_3 and FA. The course of the thermogram in Fig. S2 is precisely the same, indicating that the IL is unchanged by confinement inside the silica.

The coated fibres containing silica and IL was incorporated into a gas chromatography setup to undergo processes of extraction and thermal desorption. The area with the highest likelihood of damage to the fibres is in thermal desorber in the chromatograph, where the fibres are subject to high thermal stress. Verifying the practical usefulness of the fibre consisted of cycles of heating in a gas chromatograph desorber in 220° C, in a Helium atmosphere, and visual assessment of the fibres every ten cycles. The lifetime of the particular fibres were equal to 80 sorption/desorption cycles. The lifetime of the fiber was determined based on two parameters: visual assessment, where the criterion was the formation of cracks and loss of a part of the coating, the second parameter was the monitoring of the amount of retained analytes - the extraction efficiency of the fiber. The latter method of verification is because it is not possible to visually assess whether there has been any loss of ionic liquid from the pores of the material. The criterion was adopted that the loss of efficiency below 80% of the initial value disqualifies the given fiber from further use; finally, on average, a fiber lifetime of 80 sorption/desorption cycles was observed.

3.5. *Utilization of the obtained fiber for the extraction of VOCs*

The final stage of the performed research has included the utilization of ionic liquid confined SPME fiber coatings in model extractions. The extraction of a set of volatile analyses of different polarities was done from the headspace of an aqueous samples. The aim of that step was to examine the usability of prepared fibers, neither to control the optimal extraction conditions. The experiments were performed maintaining typical conditions, determined based on the available literature: desorption time 10 min, desorption temperature 220 °C, extraction time 30 min, extraction temperature 45 °C, salt concentration 20% (Na_2SO_4), sample volume 12 ml, analytes concentration in range from 5 up to 100 ppm [4].

Taking into account the Fig. 5., the total sum of the peak areas for silica fiber with confined IL in pores structure is significantly higher for all analytes than the values obtained from silica fiber without ionic liquid, respectively. This observation confirms the significant absorption potential of ionic liquid as extraction medium, and also a dominant role of IL in the extraction process.

4. Conclusions

This work presents a newly developed procedure for obtaining porous material based on silica as coating on the surface of wires. The silica acts as confinement for ionic liquid and the overall novel system is used in SPME applications. Two different approaches were used in the synthesis of silica; various precursors and different pore-forming agents were applied. After selecting the optimal conditions, two systems were used, namely: K_2SiO_3 and FA and TMOS and PEO, respectively. Finally, based on the results obtained by mercury porosimetry and the packing degree of the model ionic liquid (thermogravimetric analysis), it can be concluded that better parameters were obtained for the K_2SiO_3 and FA systems. Therefore, this system was ultimately selected to produce a SPME fibres for use in analytical procedure. The method of applying silica material to the fibres does not change the physicochemical parameters of the silica. This was confirmed by mercury porosimetry, as

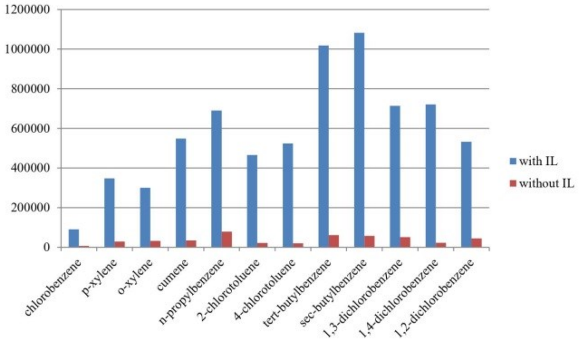

Fig. 5. Comparison of the total sum of the peak areas for silica fiber with and without confined IL in its porous structures.

the material synthesized in a test tube was compared with the material scraped off a fibres. In the silica network obtained by the sol–gel reaction of the K_2SiO_3 precursor and FA as a pore-former (1:5 v/v), an ionic liquid 1-Benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide was confined. The selection of the model ionic liquid was followed by its physicochemical properties, like high-temperature resistance indicated by thermal decomposition temperature equal to 381 °C and moderate viscosity (153 cP) [28]. Obtained SPME fibers was evaluated by the extraction of model volatile organic compounds from the headspace of an aqueous solutions. The newly obtained SPME fibres were also high thermally stable, which was confirmed by 80 cycles of sorption/desorption at 220° C in the desorber of a GC, with no changes if fibres appearance and extraction efficiency.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2022.107392.

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Supplementary Materials

Development of SPME fiber coatings with tunable porosity for physical confinement of ionic liquids as an extraction media

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Figure S1. Both sides sealed PEEK tube placed in an Eppendorf tube.

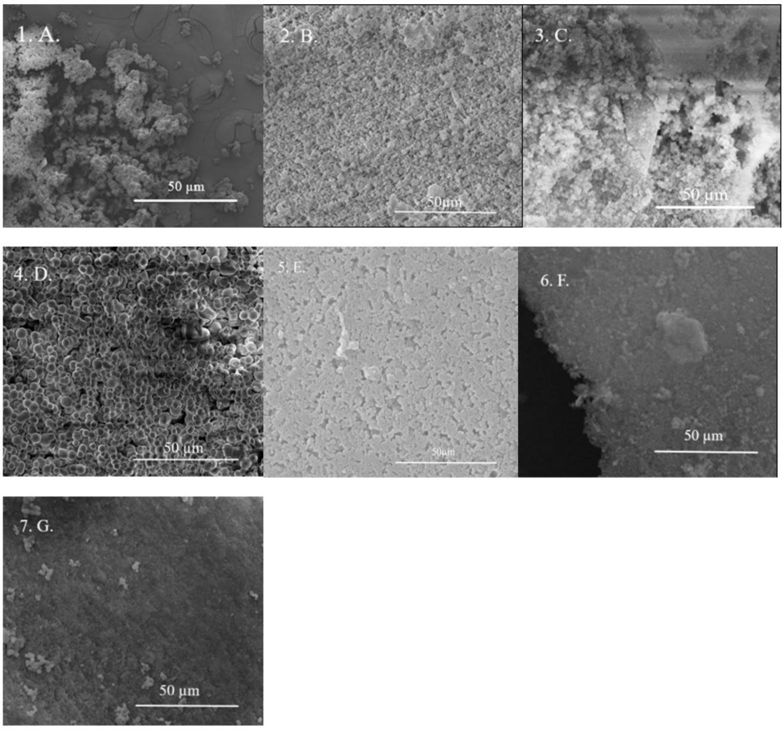

Figure S2. SEM images characterizing seven variants of TMOS and PEO synthesis. Where the A. corresponds to the 1st variant from the Table 1., B. 2, C. 3, D. 4, E. 5, F. 6, G. 7.

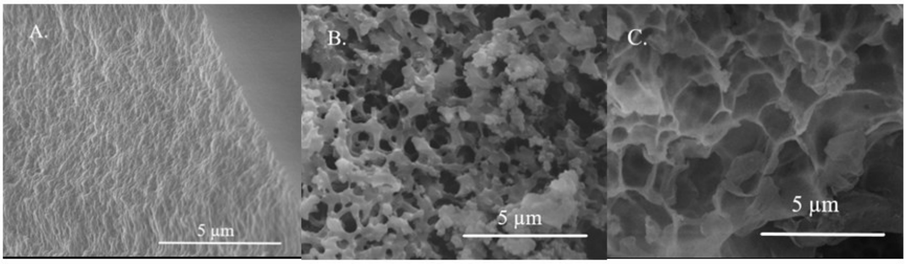

Figure S3. SEM micrographs of K_2SiO_3 and FA, where A - 1:2, B – 1:5, C – 1:10 FA to precursor, respectively.

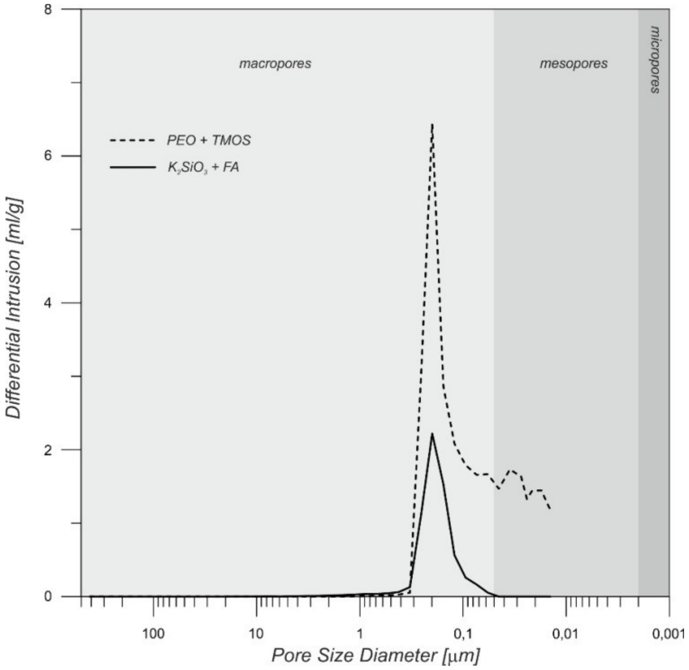

Figure S4. Differential intrusion vs pore size. Pore size classification acc. to IUPAC.

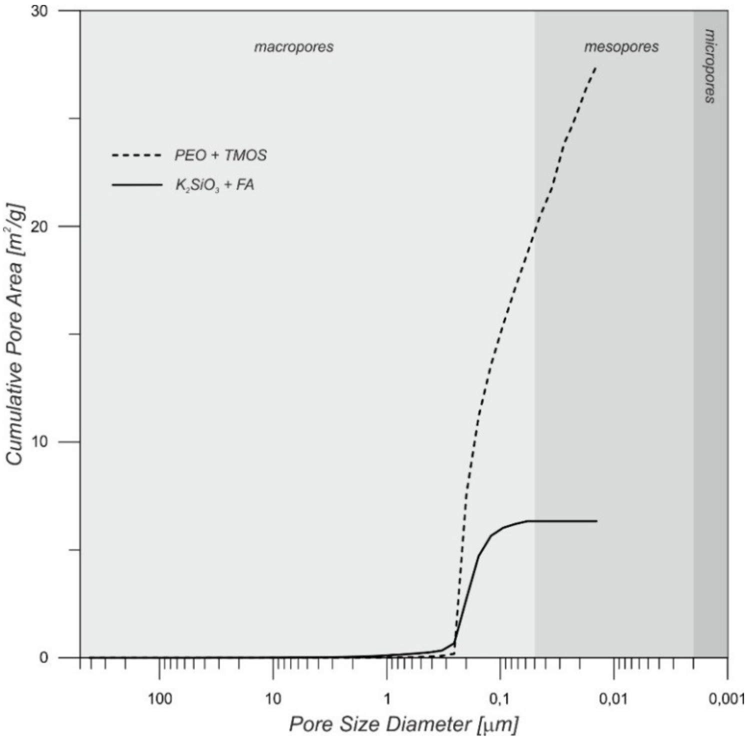

Figure S5. Cumulative pore area versus pore size. Pore size classification acc. to IUPAC.

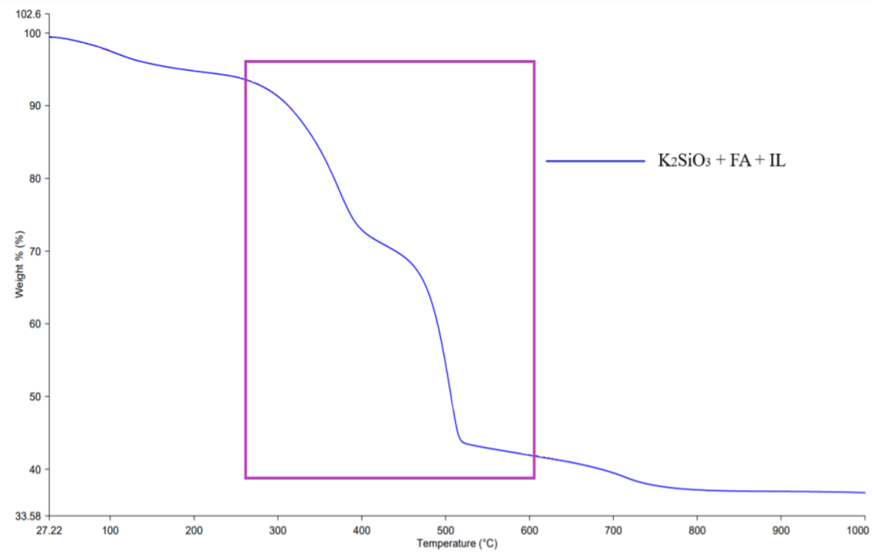

Figure S6. Thermogravimetric analysis of K_2SiO_3 + FA + IL.

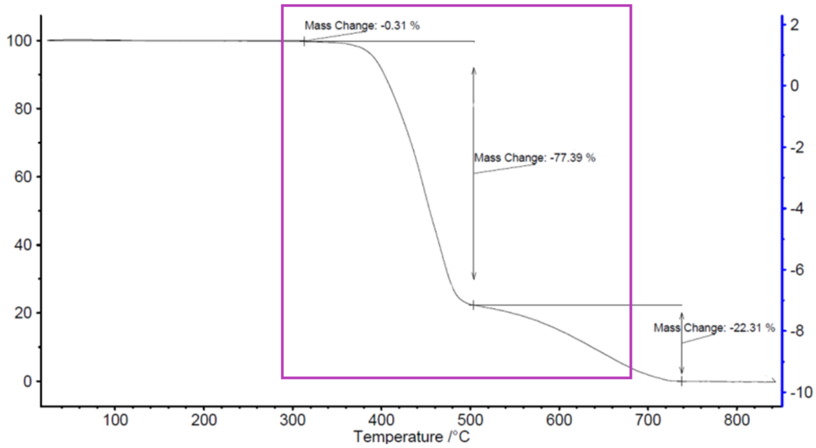

Figure S7. Thermogravimetric analysis of pure ionic liquid, namely 1-Benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide.

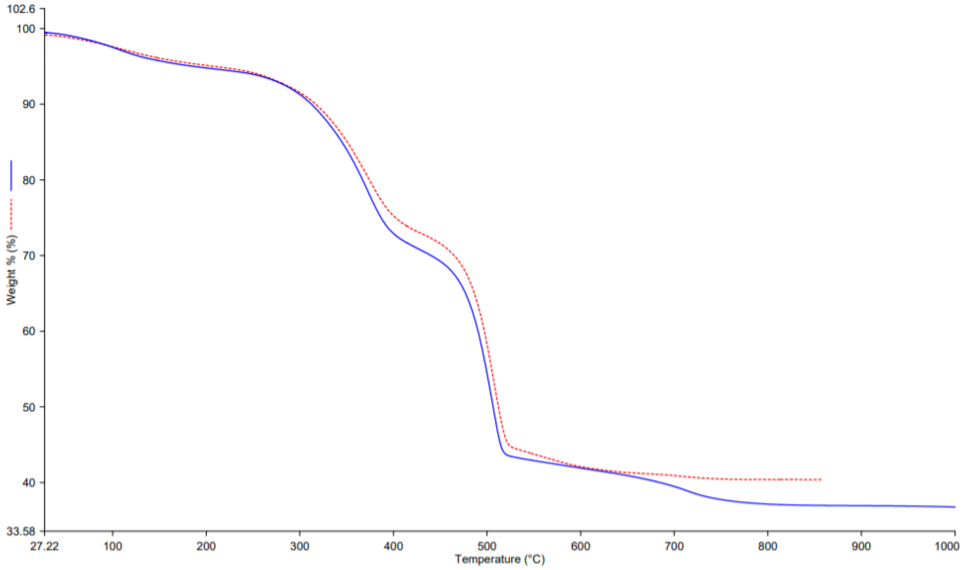

Figure S8. Thermogravimetric curves of K_2SiO_3 + FA with IL as a solid material and scratched directly from the fiber.

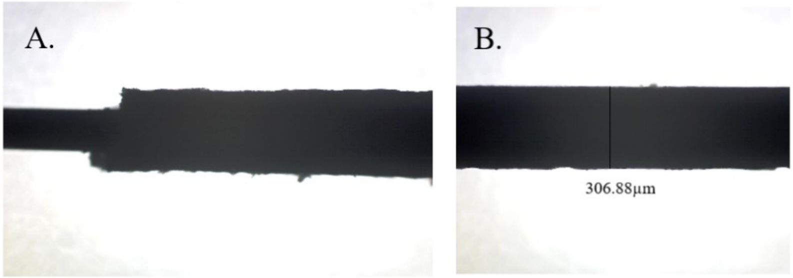

Figure S9. A. Fabricated SPME fibre at 50 times magnification. B. The diameter of the obtained fibre.

Table S1. Composition of individual samples used to synthesize a porous material.

	PEO (20 kDa) [g]	TMOS [ml]	CH_3COOH [ml]	CH_3COOH concentration [M]
1	0.1	1	2	0.01
2	0.2	1	2	0.01
3	0.3	1	2	0.01
4	0.4	1	2	0.01
5	0.2	1	1	0.02
6	0.2	1	1.5	0.013
7	0.2	1	2.5	0.008

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Załącznik 5

Head-space SPME for the analysis of organophosphorus insecticides by silica IL-based fibers in real samples

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Abstract

This work demonstrates a newly developed ionic liquid (IL)-based silica SPME fiber`s suitability for the determination of seven organophosphorus insecticides in cucumber and grapefruit samples by headspace solid-phase microextraction (HS-SPME) with gas chromatography-flame ionization detector (FID). The sol-gel method released four different sorbent coatings, which were obtained based on a silica matrix containing ILs immobilized inside its pores. In order to obtain ionogel fibers, the following ionic liquids were utilized: 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide; Butyltriethyl ammonium bis(trifluoromethylsulfonyl) imide; 1-(2-Methoxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, and 1-Benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. The developed fibers were applied for extraction of seven different insecticides from liquid samples. The most important extraction parameters of HS-SPME coupled with GC-FID method were optimized with a central composite design. The new SPME fiber demonstrated higher selectivity for extracting the analyzed insecticides compared with commercially available fibers. The limit of detection was in the range of 0.01-0.93 µg L^{-1}, coefficient of determination, which were > 0.9830, and a 4.8 – 10.1% repeatability of the method were found. Finally, the obtained ionogel fibers were utilized to determine insecticides in fresh cucumber and grapefruit juices.

Keywords: *SPME fibres; sample preparation techniques; research development, solid-phase microextraction; ionic liquid; organophosphorus insecticide; food preservation*

1. Introduction

The term pesticides covers chemical and biological substances intended to destroy or delay the development of undesirable organisms. These compounds are used mainly to protect crops against pests, fungal diseases, weeds, to combat rodents and insects during food storage, and to protect human health [1]. Pesticides can be transferred between different ecosystems. In their initial form or as derivatives, metabolites can penetrate the soil, water, atmosphere, food products, and animal feed, thus posing a threat to living organisms. One of the pesticide groups that has found widespread use in the food and agriculture industry is organophosphorus insecticides. These insecticides are chemicals that are used to kill diverse types of insects [2]. Over the last decades, the analysis of organophosphorus insecticides has appeared as a subject of a significant matter, mainly due to their potential persistence, toxicity, and water solubility [3]. The organophosphorus compounds are widely used toward pest control, demonstrating high insecticidal activity [4]. Organophosphates are readily resorbed after oral, dermal, or inhalation route of exposure [5]. The organophosphorus insecticides are of acute toxicity, contributing to irreversible inhibition of acetylcholinesterase, which is crucial for the functioning of the central nervous system, usually causing respiratory paralysis and death [6]. Therefore, there is a critical need to determine and quantify of trace level of organophosphorus insecticides in food samples [7].

Based on the available research and literature review, it was established that insecticides appear in the environmental samples in relatively low concentrations. Due to that, the extraction of insecticides may be a challenging process, requiring somewhat sensitive sample preparation and chromatographic detection techniques. Therefore, as of extreme importance is the development of sample preparation techniques compatible with the low concentration of pesticides in various complex matrices. The improvements implemented in sample preparation techniques usually concern the miniaturization, automation, and solvent-free nature of the sample preparation method, in consistency with Green Analytical Chemistry principles. Several microextraction techniques proposed to extract different groups of pesticides have been developed in the last three decades. The most commonly used sample preparation techniques towards the isolation and/or enrichment of analytes are liquid-liquid extraction (LLE) and solid-phase extraction (SPE) [8-9]. Nevertheless, the necessity concerning the reduction of the available sample preparation time and the amounts of organic solvents needed to perform the extraction of organic pollutants from environmental samples has provided the development of particular novel extraction approaches, including solid-phase microextraction (SPME) [10], and solvent microextraction [11].

The SPME is a solvent-free technique, developed by Arthur and Pawliszyn in 1990 [12]. This technique allows for the simultaneous extraction and pre-concentration of analytes in two ways: directly from an aqueous sample from the headspace above the sample. The SPME technique has gained constantly growing popularity nowadays, due to its application to the sampling of a wide range of analytes, especially from media characterized by a complex matrix composition, e.g., food or environmental samples [13-15]. Among the available sample preparation techniques, the SPME technique deserves special attention due to the many advantages: the ease of use, rapidity, the possibility of both *in-situ* and *in-vivo* sample delivery, the ease of automation, the elimination of the toxic solvent application (the "greenness" of the SPME). Nonetheless, the SPME technique is also burdened with some disadvantages, for instance, the limited lifetime of single fiber use, the restricted choice of the commercially available SPME fibers, and the possibility of SPME fibers sorption materials degradation at high temperatures during thermal desorption. Recently, a significant amount of scientific studies were focused on developing and applying new sorption materials as stationary phases as SPME fiber coatings. So far, the most commonly reported were the molecularly imprinted polymers, ionic liquids (ILs), polymeric ionic liquids (PILs), conductive polymers, nanoparticles of noble metals, and various carbon-based sorbents (graphene, single- and multi-walled carbon nanotubes) [16]. The vast majority of the mentioned SPME coatings work with adsorption mechanism (even 90%), involving some of the drawbacks, e.g., the competitive analytes phenomenon narrowed linearity of the extraction. The abovementioned limitations do not happen when "liquid-like" materials are applied since the working mechanism involved in these materials concerns the absorption mechanism. Additionally, these materials should also meet the following criteria: pose a negligible vapor pressure, occur in a liquid phase in a wide range of temperatures, and be thermally stable in relatively high temperatures. Thus, substances that fully comply with these requirements are, no doubt, ionic liquids. What is more, ILs have the possibility of being combined from different cation and anion pairs, allowing them to obtain demanded properties, thus, being called "*designer solvents*" [17-19].

The concept of the proposed work assumes obtaining a porous solid silica structure with confined ionic liquid (ionogel) on the surface of the SPME fiber. The obtained solid material is characterized by large pore volumes and diameters, allowing for as high as possible ionic liquid loading. The ILs are applied inside the material's pores through a dip-coating technique. In this work, four types of SPME fibers were prepared based on the silica matrix (K_2SiO_3 and Formamide) with the confinement of following ionic liquids: 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (IL-1); 1-Benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (IL-2); 1-(2-Methoxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (IL-3); and Butyltriethyl ammonium bis(trifluoromethylsulfonyl) imide (IL-4). The selection of these ILs has been confirmed based on their beneficial parameters differences, like high or moderate viscosity and desorption temperatures [20-21].

This work explores the practicability of tuning the extraction properties of developed ionogels with different ionic liquids to extract organophosphorus insecticides as target analytes. The developed ionogel fibers were examined by extracting insecticides from aqueous fruit and vegetable samples (grapefruit and cucumber).

2. Materials and methods

2.1. Reagent and materials

The various insecticides, including diazinon, paraoxon-ethyl, phosalone, dimethoate, fenitrothion, chlorfenvinphos, heptenophos, were purchased from Sigma-Aldrich (Germany) (Table S1). The target compounds were selected to investigate the impact of polarity and solubility in the water/octanol system on the extraction process using developed SPME fibers. Additionally, selected compounds varies significantly in terms of molecular sizes, which may have an influence on the kinetics of the extraction process. Quantitatively, the aforementioned properties were determined by pKa values (in the range 2.6 – 8.39), Log K_{ow} (in the range 0.78 – 4.38), and molar masses (in the range 229.30 – 367.81). Detailed data are collected in Table S1 in Supplementary Materials. A stock standard solution (100 mg L $^{-1}$) of each compound was prepared in acetonitrile. Further, working standard solutions were prepared by diluting the prepared stock solutions with methanol (HPLC grade, Sigma-Aldrich, Poland). The solutions were stored at 4–5°C.

2.2. Instrumentation

All analyses were carried out on a gas chromatograph Agilent Technologies 7890A GC System coupled with flame ionization detection (FID). The GC was equipped with a SPB-5 capillary column (30 m ×0.32 mm ID and 0.25 µm film thickness) that was purchased from Sigma-Aldrich (Poland). The GC temperature program commenced at 50°C for 6 min, after which it was increased successively to 300°C at 15°C min^{-1}, where it was held for 3 min. The injector (in the splitless mode) and detector were maintained at 220°C, and 300°C, respectively. Furthermore, ultrapure hydrogen (>99.99 %) was utilized as the carrier gas at a flow rate of 0.8 mL min^{-1}. The flow rates of the selected FID gases, i.e., air and nitrogen, were 400 and 30 mL min^{-1}, respectively. The SPME holder for the manual sampling and the commercially available fibers (polydimethylsiloxane (PDMS), 100 µm; polyacrylate (PA), 85 µm; were purchased from Merck (Poland).

2.3. Preparation of SPME fibers

Ionogel-based SPME fibers were prepared based on the procedure, briefly involving four steps: introduction of the hydroxy groups on the glass surface, preparation of the sol solution, sol-gel coating, and thermal treatment. The glass fiber was prepared according to the procedure reported in our work previously [22]. The ionogel sol solution was prepared from the formamide as a pore-forming agent, and K_2SiO_3 as a precursor (1:5, v/v), mixed in a plastic Eppendorf tube (10 minutes of mixing). The resulting solution was injected by the syringe into a polymeric PEEK (polyether ether ketone) tube. Then, the pre-treated glass fiber was inserted inside of the tube with the solution. To prevent the leakage of the sol solution, the bottom and the top of the tube were closed by a GC septum, and placed to the Eppendorf tubes (to avoid evaporation). Finally, after gelation, the fiber was removed from the PEEK tube and submitted to further experimental steps.

2.4.HS-SPME procedure

Six types of SPME fibers, including four ionogel fibers (1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide; Butyltriethyl ammonium bis(trifluoromethylsulfonyl) imide; 1-(2-Methoxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, and 1-Benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide)) and two commercial fibers (PDMS, PA), were utilized in this work. SPME analyses were performed using glass vials (15 mL) containing 12 mL of aqueous standard solution or water sample containing 25 % (w/w) Na_2SO_4. A glass-coated stirring bar was placed in the vial at a stirring rate of 1800 rpm, after which the vial was sealed with a Teflon-faced septum screw cap, and the solution was thermostated for 50 min at 65°C. Thereafter, 10.0 µL of the stock solution was injected into 12 mL of the aqueous solution (final pesticides concentration was equal to 83 ppb) and left for 30 min to achieve thermal equilibrium. The fiber was exposed to HS above the sample solution for 70 min at 65°C. Finally, it was removed from the vial and inserted in the GC injector port for thermal desorption at 220°C. The insecticides were thermally desorbed for 10 min.

2.5. Real samples

The fruit (grapefruit) and vegetable (cucumber) samples utilized in this study were purchased from a street market in Gdansk, Poland. At first, samples were blended, and the obtained mixtures were homogenized with a centrifuge (10 min, 4000 rpm), and then were filtered. After that, obtained juices were diluted with ultrapure water in the following percentage of fruit and vegetable concentration: 75%, 50%, 25%, and 1 % respectively. To all of the solutions the Na_2SO_4 was added, in order to obtain the optimal value of 25% (v/v). Then, 12 mL of each of examined solution, and a stir bar were placed in the 15 mL vial, sealed with a cap containing a membrane, and mixed for 20 min at room temperature. Thereafter, 10.0 µL of the insecticide mixture (100 mg L^{-1}) was spiked into the solution with continuous stirring for 30 min. Afterward, the obtained solution was thermostated for 50 min at 65°C. The extraction was performed under the optimal conditions of the obtained ionogel fibers: time,

70 min; temperature, 65°C.

3. Results and discussion

3.1. Characterization of the SPME fibers

3.1.1. Optical microscope

The thickness and regularity of the obtained fiber coating were visually evaluated by an optical microscope. As shown in Fig. 1, (exemplary) it is noticeable that obtained fiber coating is characterized as one of regular shape and thickness, smooth, with no visible cracks.

Figure 1. Fabricated SPME fibre with its diameter at 50 times magnification.

Determination of the single fiber diameter was made in regard to 11 measurements along with the fiber (every 1 mm, total length 10 mm); at the same time, the repeatability of the fiber-to-fiber preparation was determined based on the measurement of 5 fibers; in the first case, the irregularity of the coating did not exceed 5% (309µm ± 15); and the fiber-to-fiber (322µm ± 29) was 8%.

3.1.2. Scanning Electron Microscopy

The visual appearance, porosity, and the regularity of the fiber coating were also investigated by scanning electron microscopy (SEM). As shown in Fig. 2, the fiber is characterized with visible pores (with clear porosity), with a relatively smooth surface with minimum rough areas of the fiber coating. Considering that the immobilization of the ionic liquid in the pores is based on the action of capillary forces, too large pore diameter seems an undesirable property. There were no significant differences in the regularity and visual appearance of the coatings between various IL utilized for the confinement inside the SPME fiber.

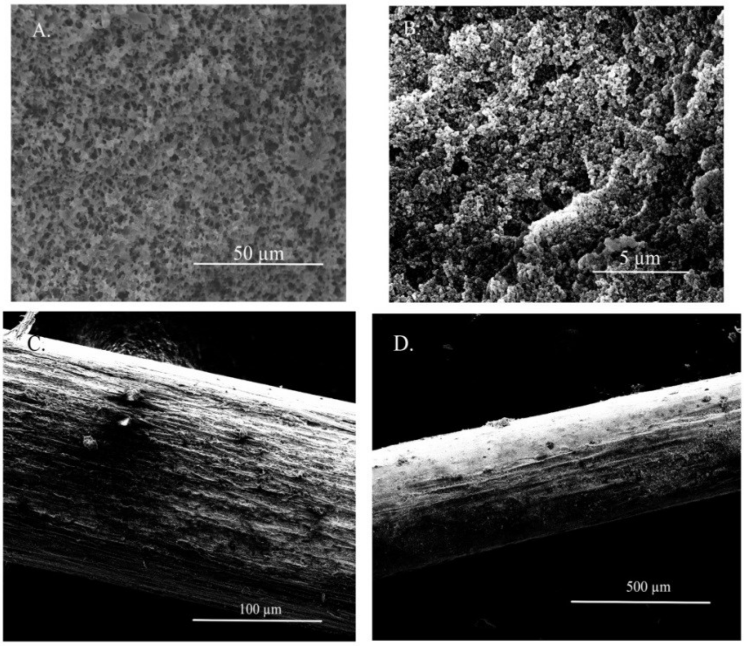

Figure 2. SEM images of the developed SPME fiber.

3.1.3. Mercury injection capillary pressure (MICP)

The material of the fiber coating was characterized by mercury intrusion porosimetry technique. The results of the measurement is shown in Fig. S1 and S2. In MICP technique were used ranges of measurable pore diameters. Based on the collected data one might notice that obtained porous material contains, virtually, only pores with diameters in the range from 0.18 µm up to 0.46 µm, with an average at 0.326 µm (Table 1). The pore diameter distribution is slightly asymmetrical with tailing towards the smaller diameters.

Table 1. Characterization of the obtained porous materials by mercury porosimetry.

Material evaluated	Median pore diameter (volume) [µm]	Median pore diameter (area) [µm]	Average pore diameter [µm]	Total pore area [m²/g]	Total porosity [%]
K_2SiO_3 + FA	0.362	0.188	0.326	6.33	50.35

3.1.4. Confinement of ionic liquid

The aim of this stage was to check the effectiveness of the process of immobilizing the ionic liquid in the pores of the silica material. The procedure was carried out in five stages: evacuating the air from the system; introducing the fiber (for 30 minutes under vacuum); holding the fiber under vacuum for 2 hours until air is removed from the pores; slowly pressure build-up to atmospheric one (pressing IL into pores); washing the fibers with methanol. The effectiveness of the immobilization of the ionic liquid in the material's pores depends on the efficiency of air removal from the pores and the viscosity of the ionic liquid.

The vacuum during the immobilization of the ionic liquid was obtained from the pump, for which the maximum negative pressure was 10^{-2} mBa. Bearing in mind that the viscosity of the liquid decreases with increasing temperature, in this step, the maximum temperature allowed was used. According to the system used, the silicone oil was used to ensure thermal contact of the ionic liquid with the heating device. The upper limit of the temperatures used was defined when the silicone oil reached the boiling point under applied vacuum conditions. This temperature was about 150°C, therefore, in the experiments, the temperature of 100°C was adopted as a safe value.

3.1.5. Thermogravimetric Analysis

The another valuable index of the SPME fiber coatings was the volume of IL confined inside the silica network. The evaluation was performed with the use of Thermogravimetric Analysis (TGA). TGA analysis was performed for porous silica material, containing ionic liquid and without it, and also for the ionic liquid itself (Fig. S3), under the following conditions: heating up to 800°C (20°C min $^{-1}$), in argon atmosphere. Since the IL was the only thermally unstable component in the studied material, it was possible to calculate the volume of ILs inside the pores of silica material. Between 350°C and 480°C, a mass drop can be observed for the sample containing IL. There is a small change in the mass drop rate around 490°C. For comparison, the pure IL was also analysed by TGA. The similar phenomenon might be noticed in the course of decomposition of pure ionic liquid which can be seen in the Figure S4. The results of the analysis were included in Supplementary Materials (Figure S4). Taking into account the mass of the sample used for TGA measurements (1.10 mg) and density of the $[C_2C_1IM][BF_4]$ (1.294 g cm^{-3} [23]) the estimated mass content of the IL confined in the pores of silica coating was c.a. 56%.

3.2. Optimization of the HS-SPME method

3.2.1. Fiber selection

In the cores of the study, four ionic liquids as an extractant were investigated. ILs share the same bis(trifluoromethylsulfonyl) imide anion, so their extraction abilities depend solely on the cation. Cations differ with regard to their polarity, starting from the less polar butyltriethyl ammonium and (IL-4) 1-Butyl-1-methylpyrrolidinium (IL-1) cations containing only C-C sigma bonds in their structures. Ionic liquid IL-3 contains an additional aromatic ring and oxygen heteroatom, while IL-2 contains two aromatic rings. Moreover, as a reference, commercial fibers with PDMS (100 µm thick), and PA (85µm thick) coatings were used. A comparison of extraction abilities of manufactured fibers and a commercial one was performed using areas of chromatographic peaks determined for investigated analytes. Based on previous experience, the parameters of the analytical procedure were as follows: 12 ml of 20% aqueous standard Na_2SO_4 solution (w/w) in a 15 ml glass vial; stirring rate at 1800 rpm; thermostating at 55°C for 20 minutes. Thereafter, 10 µL of the stock solution was injected into 12 mL of the aqueous solution and left for 30 min to achieve thermal equilibrium. The fiber was exposed to HS above the sample solution for 35 min at 55°C. Finally, it was pulled out of the vial and inserted in the GC injector port for thermal desorption at 220°C. The insecticides were thermally desorbed for 10 min [23].

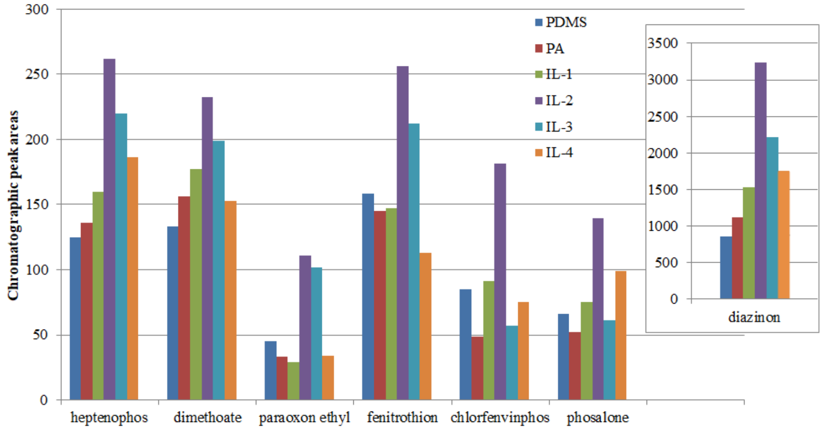

Figure 3. Comparison of the extraction abilities of investigated insecticides for different ILs, and with reference PA and PDMS commercial fibers, under optimal conditions.

Considering the differences in the volume of the coating (extractant), the areas were normalized by dividing them by the volume of the extraction phase. As can be seen in Fig. 3, the sum of peak areas for fiber with confined ionic liquids based on 1-Butyl-1-methylpyrrolidinium action (IL-2) is the highest for all investigated insecticides. The second-best fiber has pores filled with IL-2. For four of the six insecticides used, the second most effective ionic liquid was IL-3, also containing the polar 1- (2-Methoxyethyl) -3-methylimidazolium cation. Only in the case of insecticides containing a benzyl ring with a substituted chlorine atom (chlorfenvinphos, phosalone) better extraction yields were obtained with the use of non-polar fibers, both in terms of the ionic liquids and commercial coatings (PDMS) used. For this reason, fiber with a coating containing the IL-2 liquid was selected for further research.

3.2.2. Optimization of the HS-SPME procedure

Several factors, such as the extraction temperature, extraction time, equilibration time, pH of the sample, agitation conditions, salting-out effect, and headspace volume, were optimized to obtain the maximum extraction efficiency (EE) of the investigated insecticides by HS-SPME. The stirring rate was set to the maximum, 1800 rpm, purposely, to accelerate mass transfer into the system. Regarding the utilized set of insecticides, the pH was optimized within the range of 3–11. Based on the obtained results, the pH value of 7 was established as the most desirable (Fig. 4D and 4E). The HS sample volume was kept at the minimum possible (the highest aqueous sample/HS volume ratio) [24], making possible to expose the fiber at ~1.5 cm from the top of the vial. The equilibration of insecticides in the aqueous sample was performed in five-set of times: 20, 35, 50, 65, and 80 minutes. Obtained results have indicated that an equilibration time of 50 minutes was considered sufficient (Fig. 4A, 4B, and 4C). Further, the selected concentration of Na_2SO_4 was between 5 % and 25 % (w/w). The salt-effect on the extraction performance is shown in Fig. 4F. Regarding the obtained results, 25 % (w/w) of Na_2SO_4 concentration was chosen as the optimum one of the salt content in the sample for further experiments. The extraction time was optimized in the range of 30-110 minutes. Since the analytes are released from the fiber by the thermal desorption process, the thermal stability of the developed fiber is another parameter that must be considered. Due to that, the developed fibers were exposed to the GC inlet port up to the temperature of 240°C. As a result, there were no peaks of the unknown origin (artifacts) in blank runs of the analysis performed. the desorption temperature was set at 220°C, as it is 20°C less than the maximum allowable temperature to be used. Following these conditions, the carry-over effects have been studied, allowing to set 10 minutes as the optimum time for the desorption process. To reduce the number of experiments and optimize factors that can influence the extraction efficiency, the design of experiments (DoE), (Fig. S3) was utilized. What is more, applied approach provided also the possibility of interdependence amongst the input variables, which are not involved to the "one-variable-at-a-time" methodology. The extraction parameters, i.e., the time and temperature, were optimized by a central composite design (CCD). The plan was made by random sampling employing the Statistica 12 software (StatSoft, USA). The CCD plan utilizing different optimized parameters and the corresponding response variables (the sum of the chromatographic peak areas of investigated insecticides) are presented in Table S3, and Fig. 4. The significance of the standardized effects of the variables' was examined by the analysis of variance (ANOVA) method.

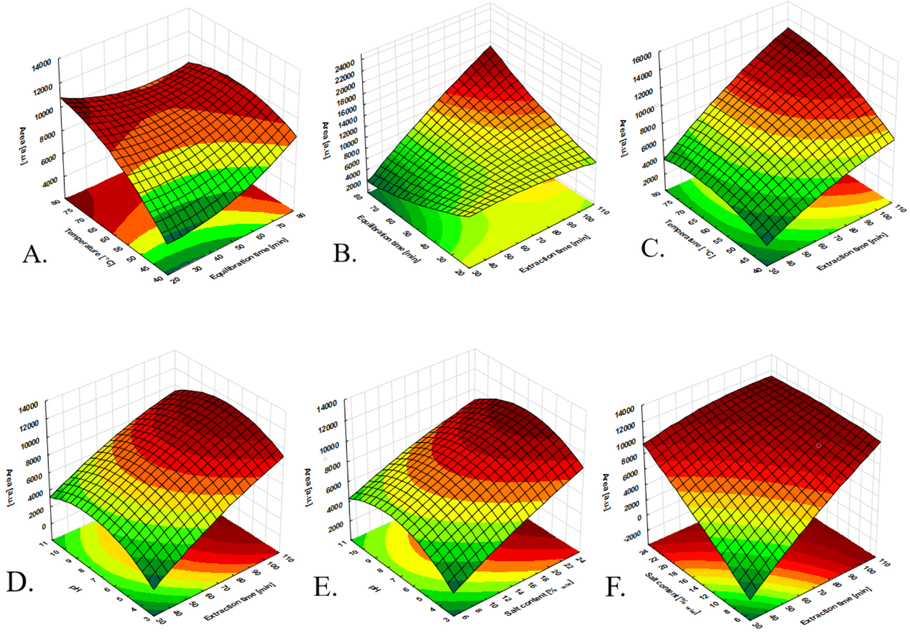

Figure 4. Statistical significance of the effects of the extraction parameters on extraction performance of the IL-based fiber: A - response surfaces as functions of extraction temperature vs. equilibration time; B - response surfaces as functions of equilibration time vs. extraction time; C - response surfaces as functions of temperature vs. extraction time; D - response surfaces as functions of pH vs. extraction time; E - response surfaces as functions of pH vs. salt content; F - response surfaces as functions of salt content vs. extraction time.

3.2.3. Method validation

The performances of the HS-SPME–GC-FID method regarding the single fiber and fiber-to-fiber repeatabilities, limits of detection (LOD), limits of quantification (LOQ), and linearity of the calibration curve (R^2, slope, and intercept) were evaluated under the optimized experimental conditions. The repeatabilities, LODs, and R^2s of IL-2-based ionogel fiber are presented in Table 3.

Table 3. Analytical characteristics of the developed HS-SPME-GC-FID method for organophosphorus insecticides determination using investigated silica-IL fiber.

Compound	LOD	LOQ	Correlation coefficient	Repeatability of single fiber	Repeatability of fiber-to-fiber
Heptenophos	0.21	0.63	0.9931	6.4	13.4
Dimethoate	0.50	1.50	0.9925	6.1	14.8
Diazinon	0.01	0.03	0.9956	4.8	12.1
Paraoxon-ethyl	0.60	1.80	0.9850	9.6	12.7
Fenitrothion	0.05	0.15	0.9832	10.1	13.7
Chlorfenvinphos	0.10	0.30	0.9911	7.4	15.5
Phosalone	0.93	2.79	0.9847	8.2	16.4

The concentrations of the insecticides ranged from 0.01–83 µg/L. The calibration curves of all the analytes were linear within the ranges starting at the LOQ level, with the lowest value of 0.9832 obtained for fenitrothion. LODs of the ionogel fibers were calculated as a signal-to-noise ratio of 3, as specified in Table 3 , and were in the ranges of 0.01– 0.93 µg/L. The calculated LOQs (signal-to-noise ratio of 9) were in the ranges of 0.03–2.79 µg/L.

The repeatability of a single fiber (Table 3) describes the repeatability of the HS-SPME–GC-FID method for the same fiber in five replicates of the extraction. The highest relative standard deviation (RSD) of the repeatability was found for fenitrothion and equals 10.1, which is an acceptable level. The fiber-to-fiber repeatability is a test of the applicability of the proposed procedure to obtain identical ionogel fibers. Here, the obtained RSDs were between 12.1 % and 16.4 % for diazinon and phosalone, respectively. The performance of each type of the obtained ionogel fiber began to decrease after c.a. 60 extraction/desorption cycles. Therefore, a total of 60 cycles was selected as the lifetime of the fiber.

3.3. Real sample analysis

In the final stage of the evaluation of the developed ionic liquid - based SPME fiber coatings, prepared fibers were utilized in real samples extractions. The extraction of a set of organophosphorus insecticides was performed from the headspace of water, cucumber and grapefruit samples.

The matrix effect was assessed on the basis of the change in extraction efficiency depending on the degree of juice dilution. Four dilutions were used, with the sample juice content being 50, 25, 10, and 1 % by volume. Additionally, extractions from the headspace of fresh juice samples were performed. Experiments were performed under optimized conditions. The determined dependences of the relative recovery for the investigated insecticides as a function of the dilution of the original juice samples are presented in the Figure 5 (grapefruit), and 6 (cucumber).

Extraction results from water samples were used as the reference point. As can be seen in both cases, the matrix effect is significant, where the reduction of the extraction efficiency ranges from 20 to 60% and from 20 to 70% for grapefruit and cucumber juice, respectively. In the case of cucumber juice with a juice content of 10%, only for chlorfenvinphos the relative yield was lower than 90%. At the same time, achieving a similar RR level for the grapefruit sample required a 100-fold dilution of the sample. However, it can be expected that the influence of the matrix mostly concerns the partitioning of the analytes between the sample and the headspace. This assumption may be confirmed by the results published by other authors, where various types of extraction coatings were used [25].

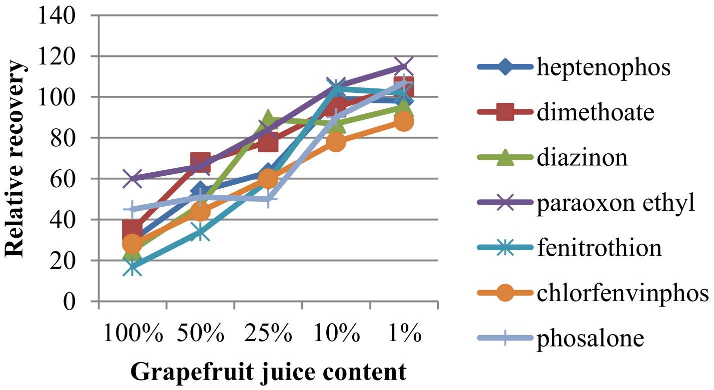

Figure 5. Effect of diluting the samples with ultrapure water at different dilution ratios (v/v) utilizing the IL-2 fiber for extraction of grapefruit juice.

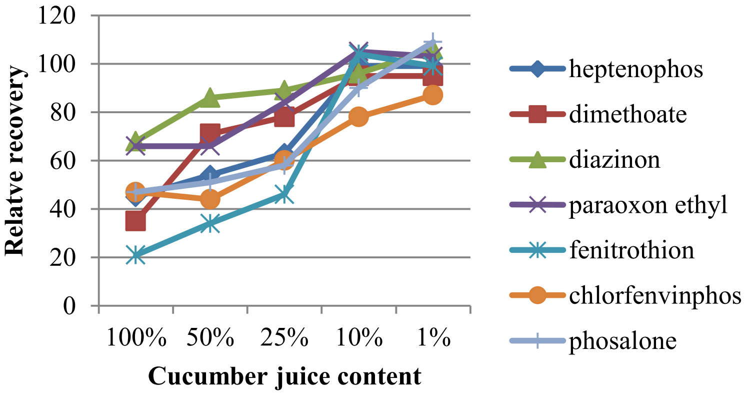

Figure 6. Effect of diluting the samples with ultrapure water at different dilution ratios (v/v) utilizing the IL-2 fiber for extraction of cucumber juice.

3.4. Comparison with other pesticides determination methods

The HS-SPME-GC-FID method was compared with the other previously published methods to determine target organophosphorus insecticides in water, cucumber, and grapefruit juice samples. Table 4 summarizes LOD, RSD, R^2, RR, extraction time, and type of extractant applied of several analytical techniques investigated so far by scientists towards determination of the selected insecticides. Table 4 includes analytical procedures covering a wide range of extraction technique, and final determination methods. Notably, LODs and RSD for the proposed method were comparable or better with those of other methods. Additionally, there is no significant difference also in R^2 values. What is more, investigation of a compiled procedures using a combination of SPE and DLLME with MS detection allows gaining much lower LOD than described in this work.

Based on the results, HS-SPME-GC-FID method is an easy, fast, sensitive, and repeatable method that can be used towards determination of selected insecticides in diverse matrices.

Table 4. Comparison of the proposed HS-SPME-GC-FID method with other methods available in the literature, dedicated to determination of investigated in this work insecticides.

Analyte	Method	Sample	Real/ standard[1]	Extraction phase used	LOD (µg*L^{-1})	RSD (%)	Extraction time (min)	Relative recovery	R^2	Ref.
Diazinon, Fenitrothion	HS-SPME-GC-FID	Apple and carrot juices	Real	Ionogel [Set3, C_4C_1Pip, and Set3/C_4C_1Pip]	0.01-0.95	2.2-7.4	60	77-114	0.9108-0.9992	[23]
Diazinon	MSPE-DLLME-GC-FID[2]	Fruit, vegetable, and nectar	Real	$Fe_3O_4@SiO_2@ph$	0.26	5	2 and 5	100-106	0.9988	[26]
Diazinon	CHLLE-DLLME-GC-FID[3]	Fruit and vegetable juices	Standard	Di-iso-butyl amine	0.32	6	4	75-99	0.998	[27]
Diazinon, Fenitrothion	MSPE-GC-FID[4]	Water and fruit juices	Real	KHA/Fe_3O_4	0.07-0.14	6.5-8.1	5	89.3-97.3	0.9910-0.9981	[28]
Fenitrothion, Diazinon	SPME-DLLME-GC-MS[5]	Water, honey, orange and milk	Standard	C18	0.0005-0.001	0.4-4.71	1	78-98	0.9941-0.9996	[29]
Paraoxon-ethyl	MDCG-MS-DI-SPME[6]	Peach, orange and pineapple	Real	PA 65µm with a layer of PDMS/DVB	n.a.	0.37	60	n.a.	0.9989	[30]
Heptenophos, dimethoate, diazinon, paraoxon ethyl, fenitrothion, chlorfenvinphos, phosalone	HS-SPME-GC-FID	Water, cucumber and grapefruit juice	Real	Ionic liquid	0.01-0.93	4.8-10.1	70	85-118	0.9832-0.9956	This work

[1] – The presented LOD values were calculated for real or standard samples (pure water) in the original articles.
[2] – Magnetic solid-phase extraction-dispersive liquid-liquid microextraction-gas chromatography-flame ionization detection.
[3] – Continuous homogenous liquid-liquid extraction-dispersive liquid-liquid microextraction-gas chromatography-flame ionization detection.
[4] - Magnetic solid-phase extraction-gas chromatography-flame ionization detection.
[5] – Solid-phase extraction-dispersive liquid-liquid microextraction-gas chromatography-mass spectrometry.
[6] – Multidimensional gas chromatography-mass spectrometry- direct injection- solid-phase microextraction.

Conclusions

The HS-SPME GC-FID method was successfully applied to determine the presence of selected organophosphorus insecticides in fruit and vegetable samples. Four different IL-based fibers were investigated in this work (IL-1; IL-2; IL-3; and IL-4). The IL-based fibers were obtained by the deep-coating technique, which involved the immersion of glass fibers in a mixture of K_2SiO_3 and FA, in which the listed ILs were confined separately.

After optimizing the main extraction parameters of each fiber, the sums of the total peak areas were compared. The SPME coating made with IL-2 exhibited the best extraction efficiency results. The research has shown that the extraction efficiency can be influenced by the selection of IL. Further, by selecting a different IL to be confined, it is possible to simply and conveniently tune the required physicochemical properties of ILs, depending on the class of substances to be extracted. The results indicated that the total sum of the peak areas was higher for the proposed ionogel fibers than for commercially available (PDMS and PA). The ionogel coatings achieved promising results for their application as extractants for SPME. Finally, the proposed ionogel fibers were employed to analyze the insecticides in fresh apple and carrot juices. It was revealed that the sample matrix could affect the extraction efficiency of SPME of insecticides.

Acknowledgements

The authors are indebted to Gabriela Nowak-Wiczk MSc (University of Gdańsk) for thermogravimetric analysis measurements and Aleksandra Mielewczyk-Gryń PhD (Gdańsk University of Technology) for scanning electron microscopy measurements. We would like to thank Grzegorz Machowski (AGH University of Kraków) for the performance of the MICP measurements of the investigated samples.

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Supplementary Materials

Head-space SPME for the analysis of organophosphorous insecticide by silica IL-based fibers in real samples

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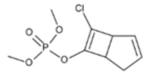
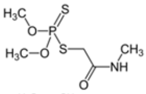
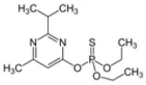
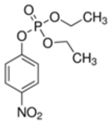
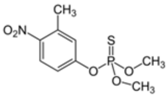
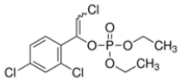
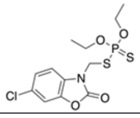
Table S1. Physicochemical properties of the studied insecticides.

Compound	Structure	pKa value	molecular weight [g/mol]	CAS number	$\log K_{ow}$
heptenophos		2.72	250.61	23560-59-0	2.32
dimethoate		0.78	229.3	60-51-5	0.78
diazinon		3.11	304.35	333-41-5	3.30
paraoxon ethyl		1.98	275.19	311-45-5	1.98
fenitrothion		n.a.	277.23	122-14-5	3.30
chlorfenvinphos		4.70	359.6	470-90-6	3.81
phosalone		4.38	367.81	2310-17-0	4.38

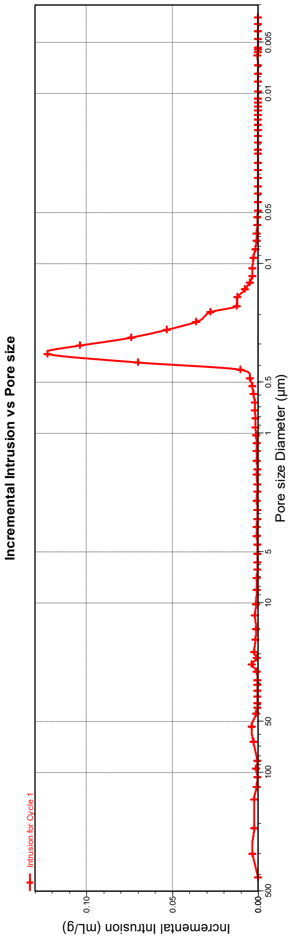


Figure S1. Mercury Intrusion Porosimetry: Plot of incremental intrusion vs. pore size. The measurement was performed with the use of AutoPore IV 9500 V1.09 Micrometrics Instrument Corporation.

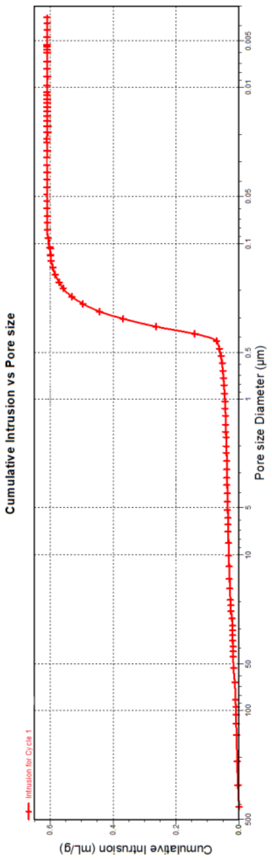
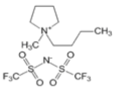
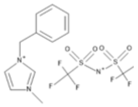
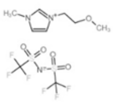
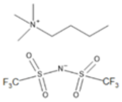


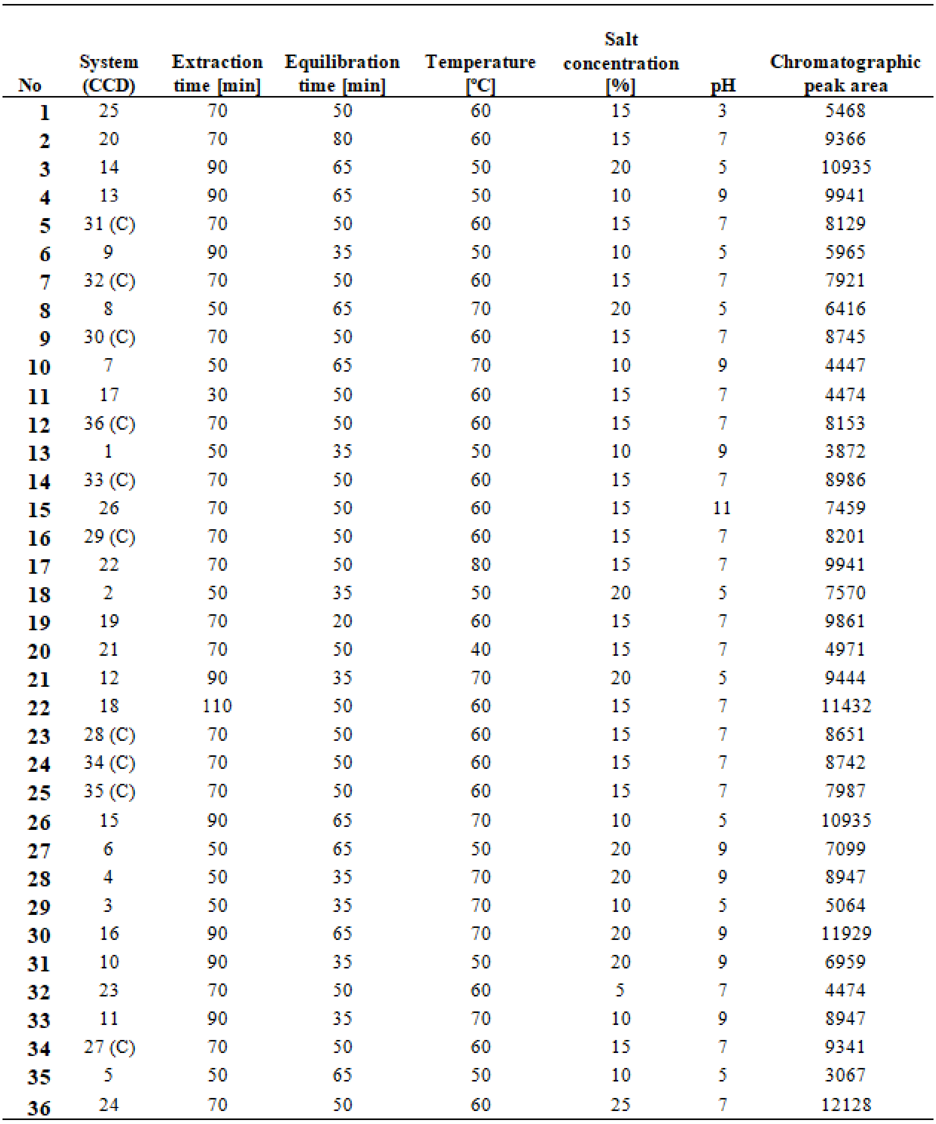
Figure S2. Mercury Intrusion Porosimetry: Cumulative intrusion vs. pore size. The measurement was performed with the use of AutoPore IV 9500 V1.09 Micrometrics Instrument Corporation.

Table S2. Physicochemical properties of the studied ionic liquids.

Ionic liquid (IL)	IL structure	Acronym of IL	MW	Tm	Td	d	η	CAS
1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide		IL-1	422.4	<RT	360	1.40	95	223437-11-4
1-Benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide		IL-2	208.69	<RT	396	1.49	135	433337-24-7
1-(2-Methoxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl) imide		IL-3	421.34	<RT	358	n.a.	46.9	178631-01-1
Butyltriethyl ammonium bis(trifluoromethylsulfonyl) imide		IL-4	369.4	<RT	>220	1.39	99.5	258273-75-5

^{a} MW – molecular weight;
^{b} T_m – melting point[°C];
^{c} T_d – decomposition temperature[°C];
^{d} d – density $[g*cm^3]$;
^{e} η – viscosity [cP];
CAS – CAS number

Table S3. CCD plan and responses (sum of the peak areas), which were obtained to extract the insecticides with the investigated IL-2 based fiber.



No	System (CCD)	Extraction time [min]	Equilibration time [min]	Temperature [°C]	Salt concentration [%]	pH	Chromatographic peak area
1	25	70	50	60	15	3	5468
2	20	70	80	60	15	7	9366
3	14	90	65	50	20	5	10935
4	13	90	65	50	10	9	9941
5	31 (C)	70	50	60	15	7	8129
6	9	90	35	50	10	5	5965
7	32 (C)	70	50	60	15	7	7921
8	8	50	65	70	20	5	6416
9	30 (C)	70	50	60	15	7	8745
10	7	50	65	70	10	9	4447
11	17	30	50	60	15	7	4474
12	36 (C)	70	50	60	15	7	8153
13	1	50	35	50	10	9	3872
14	33 (C)	70	50	60	15	7	8986
15	26	70	50	60	15	11	7459
16	29 (C)	70	50	60	15	7	8201
17	22	70	50	80	15	7	9941
18	2	50	35	50	20	5	7570
19	19	70	20	60	15	7	9861
20	21	70	50	40	15	7	4971
21	12	90	35	70	20	5	9444
22	18	110	50	60	15	7	11432
23	28 (C)	70	50	60	15	7	8651
24	34 (C)	70	50	60	15	7	8742
25	35 (C)	70	50	60	15	7	7987
26	15	90	65	70	10	5	10935
27	6	50	65	50	20	9	7099
28	4	50	35	70	20	9	8947
29	3	50	35	70	10	5	5064
30	16	90	65	70	20	9	11929
31	10	90	35	50	20	9	6959
32	23	70	50	60	5	7	4474
33	11	90	35	70	10	9	8947
34	27 (C)	70	50	60	15	7	9341
35	5	50	65	50	10	5	3067
36	24	70	50	60	25	7	12128

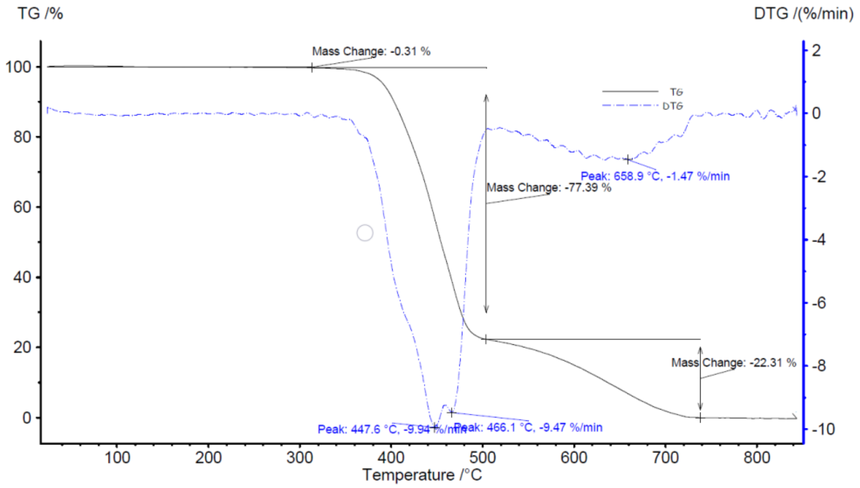


Figure S3. Thermogravimetric curves of K_2SiO_3 + FA with IL as a solid material of the fiber.

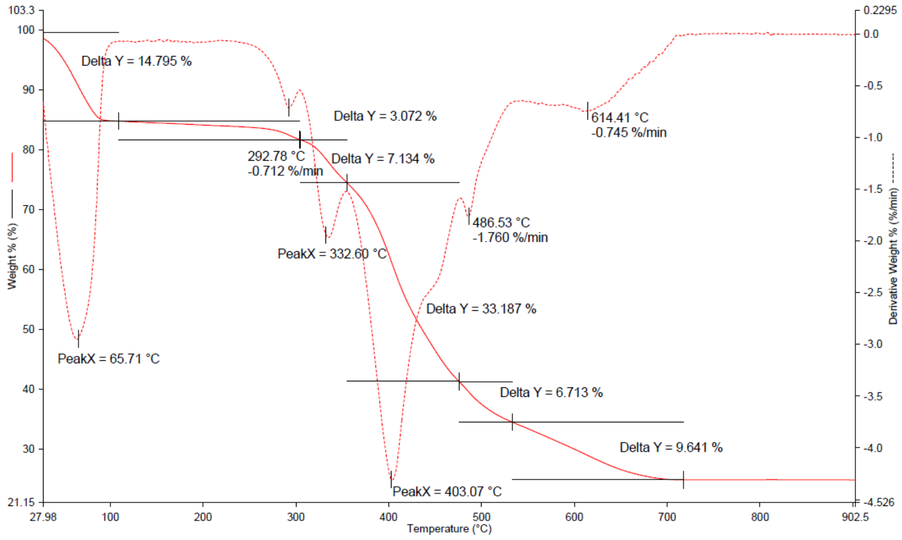


Figure S4. Thermogravimetric analysis of pure ionic liquid, namely 1-Benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide.

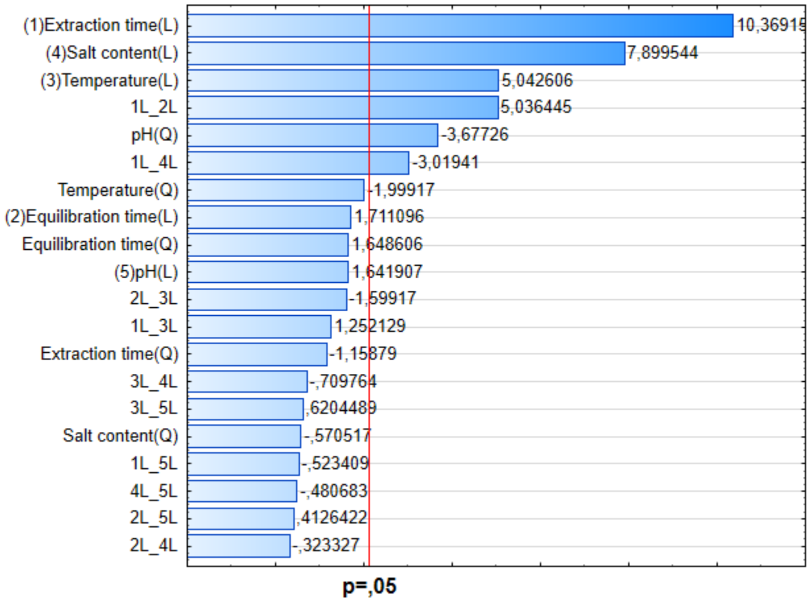


Figure S5. Statistical significance of the effects of the extraction parameters on extraction performance of the IL-based fiber: standardized effect Pareto chart.

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LISTA OSIĄGNIĘĆ NAUKOWYCH

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WYDZIAŁ CHEMICZNY

Publikacje w czasopismach z listy JCR

[1] R. Marcinkowska, **K. Delińska (Konieczna)**, Ł. Marcinkowski, J. Namieśnik, A. Kloskowski, Application of ionic liquids in microextraction techniques: Current trends and future perspectives, TrAC Trends in Analytical Chemistry (2019) 119, 115614. Q1, IF 9.801, DOI: 10.1016/j.trac.2019.07.025

[2] K. Yavir, **K. Delińska (Konieczna)**, Ł. Marcinkowski, A. Kloskowski, Ionic liquids in the microextraction techniques: The influence of ILs structure and properties, Trends in Analytical Chemistry (2020) 130, 115994, DOI: 10.1016/j.trac.2020.115994

[3] K. Yavir, **K. Delińska (Konieczna),** Ł. Marcinkowski, A. Kloskowski, Tuning the extraction properties of ionogel-coated Solid-phase microextraction fibers based on the solvation properties of the ionic liquids, Separation and Purification Technology (2020) 247, 116988. Q1, IF 7.278, DOI: 10.1016/j.seppur.2020.116988

[4] **K. Delińska (Konieczna),** K. Yavir, M. Kermani, A. Mielewczyk-Gryń, A. Kloskowski, The new silica-based coated SPME fiber as universal support for the confinement of ionic liquid as an extraction medium, Separation and Purification Technology (2020) 252, 117411. Q1, IF 7.278, DOI: 10.1016/j.seppur.2020.117411

[5] **K. Delińska**, P. W. Rakowska, A. Kloskowski, Porous material-based sorbent coatings in solid-phase microextraction technique: Recent trends

and future perspectives, TrAC Trends in Analytical Chemistry (2021) 143 116386. Q1, IF 12.296, DOI: 10.1016/j.trac.2021.116386

[6] **K. Delińska**, K. Yavir, A. Kloskowski, Ionic liquids in extraction techniques: Determination of pesticides in food and environmental samples, Trends in Analytical Chemistry (2021) 143, 116396. Q1, IF 12.296, DOI: 10.1016/j.trac.2021.116396

[7] **K. Delińska**, G. Machowski, A. Kloskowski, Development of SPME fiber coatings with tunable porosity for physical confinement of ionic liquids as an extraction media, Microchemical Journal (2022) 107392. Q2, IF 4.821, DOI: 10.1016/j.microc.2022.107392

[8] **K. Delińska**, K. Yavir, A. Kloskowski, Head space for the analysis of organophosphorous insecticides by silica IL-based fibers in real samples, Molecules. Q1, IF 4.412, w recenzji.

Inne publikacje:

[1] **K. Konieczna**, Ł. Marcinkowski, A. Kloskowski, J. Namieśnik, Ciecze jonowe jako medium sorpcyjne w mikroekstrakcji do pojedynczej kropli. Cz. II. Praktyka analityczna, Analityka: Nauka i praktyka, Warszawa (2019) 12-17

[2] **K. Konieczna**, Ł. Marcinkowski, A. Kloskowski, J. Namieśnik, Ciecze jonowe jako medium sorpcyjne w mikroekstrakcji do pojedynczej kropli. Cz. I. Podstawy teoretyczne i zagadnienia. Analityka: Nauka i praktyka, Warszawa (2019) 30-34

Prezentacje na konferencjach naukowych

1. Development of a universal silica-based matrix for immobilization of ionic liquids used as sorption materials in the solid-phase microextraction technique. **Karolina Konieczna,** Łukasz Marcinkowski, Adam Kloskowski. 4th International Conference on Ionic Liquids in Separation and Purification Technology, Sitges, Hiszpania (8.09-11.09.2019). – wystąpienie ustne.

Stypendia naukowe

2019 – 2022	Stypendium Rektora Politechniki Gdańskiej dla najlepszych doktorantów
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OŚWIADCZENIA O UDZIALE W PUBLIKACJACH

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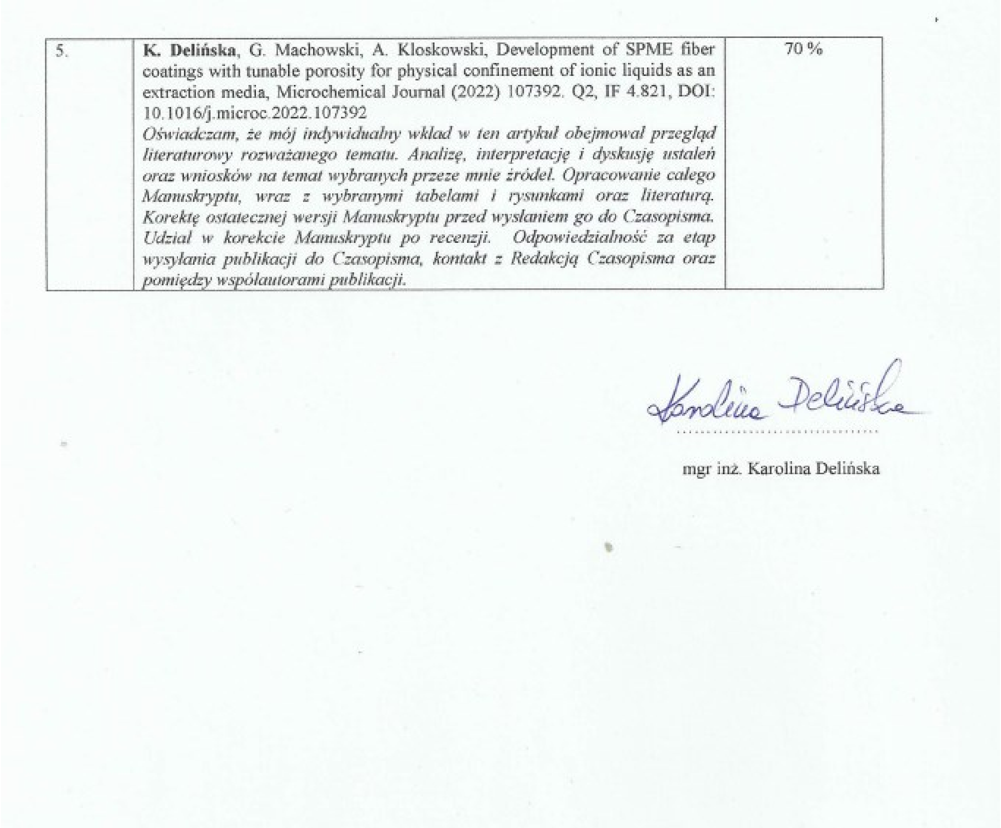
Gdańsk, 15.06.2022

Oświadczenie o udziale w publikacji

Lp.	Publikacja	Udział procentowy
1.	R. Marcinkowska, **K. Delińska (Konieczna)**, Ł. Marcinkowski, J. Namieśnik, A. Kloskowski, Application of ionic liquids in microextraction techniques: Current trends and future perspectives, TrAC Trends in Analytical Chemistry (2019) 115614. Q1, IF 9.801, DOI: 10.1016/j.trac.2019.07.025 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował przegląd literaturowy rozważanego tematu. Przygotowałam Rozdział 4, streszczenie, skróty i akronimy, literaturę oraz tabelę 2 i wybrane rysunki. Udział w korekcie manuskryptu po recenzji.*	30 %
2.	**K. Delińska (Konieczna),** K. Yavir, M. Kermani, A. Mielewczyk-Gryń, A. Kloskowski, The new silica-based coated SPME fiber as universal support for the confinement of ionic liquid as an extraction medium, Separation and Purification Technology (2020) 117411. Q1, IF 7.278, DOI: 10.1016/j.seppur.2020.117411 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował przegląd literaturowy rozważanego tematu. Analizę, interpretację i dyskusję ustaleń oraz wniosków na temat wybranych przeze mnie źródeł. Opracowanie całego Manuskryptu, wraz z tabelami i rysunkami oraz literaturą. Korektę ostatecznej wersji Manuskryptu przed wysłaniem go do Czasopisma. Udział w korekcie Manuskryptu po recenzji. Odpowiedzialność za etap wysyłania publikacji do Czasopisma, kontakt z Redakcją Czasopisma oraz kontakt pomiędzy współautorami.*	50 %
3.	**K. Delińska**, P. W. Rakowska, A. Kloskowski, Porous material-based sorbent coatings in solid-phase microextraction technique: Recent trends and future perspectives, TrAC Trends in Analytical Chemistry (2021) 116386. Q1, IF 12.296, DOI: 10.1016/j.trac.2021.116386 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował przegląd literaturowy rozważanego tematu. Analizę, interpretację i dyskusję ustaleń oraz wniosków na temat wybranych przeze mnie źródeł. Opracowanie całego Manuskryptu, wraz z tabelami i rysunkami oraz literaturą. Korektę ostatecznej wersji Manuskryptu przed wysłaniem go do Czasopisma. Udział w korekcie Manuskryptu po recenzji. Odpowiedzialność za etap wysyłania publikacji do Czasopisma, kontakt z Redakcją Czasopisma.*	70 %
4.	**K. Delińska**, K. Yavir, A. Kloskowski, Head space for the analysis of organophosphorous insecticides by silica IL-based fibers in real samples, Molecules. Q1, IF 4.412, w recenzji. *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował przegląd literaturowy rozważanego tematu. Analizę, interpretację i dyskusję ustaleń oraz wniosków na temat wybranych przeze mnie źródeł. Opracowanie całego Manuskryptu, wraz z wybranymi tabelami i rysunkami oraz literaturą. Korektę ostatecznej wersji Manuskryptu przed wysłaniem go do Czasopisma. Udział w korekcie Manuskryptu po recenzji. Odpowiedzialność za etap wysyłania publikacji do Czasopisma, kontakt z Redakcją Czasopisma.*	70 %



5.	**K. Delińska**, G. Machowski, A. Kloskowski, Development of SPME fiber coatings with tunable porosity for physical confinement of ionic liquids as an extraction media, Microchemical Journal (2022) 107392. Q2, IF 4.821, DOI: 10.1016/j.microc.2022.107392 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował przegląd literaturowy rozważanego tematu. Analizę, interpretację i dyskusję ustaleń oraz wniosków na temat wybranych przeze mnie źródeł. Opracowanie całego Manuskryptu, wraz z wybranymi tabelami i rysunkami oraz literaturą. Korektę ostatecznej wersji Manuskryptu przed wysłaniem go do Czasopisma. Udział w korekcie Manuskryptu po recenzji. Odpowiedzialność za etap wysyłania publikacji do Czasopisma, kontakt z Redakcją Czasopisma oraz pomiędzy współautorami publikacji.*	70 %

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Gdańsk, 15.06.2022

Oświadczenie o udziale w publikacji

Lp.	Publikacja	Udział procentowy
1.	R. Marcinkowska, K. Delińska (Konieczna), Ł. Marcinkowski, J. Namieśnik, **A. Kloskowski**, Application of ionic liquids in microextraction techniques: Current trends and future perspectives, TrAC Trends in Analytical Chemistry (2019) 115614. Q1, IF 9.801, DOI: 10.1016/j.trac.2019.07.025 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował analizę rozważanego tematu. Przygotowałem rozdział dotyczący właściwości fizykochemicznych cieczy jonowych. Udział w korekcie manuskryptu przed i po recenzji.*	15 %
2.	K. Delińska (Konieczna), K. Yavir, M. Kermani, A. Mielewczyk-Gryń, **A. Kloskowski**, The new silica-based coated SPME fiber as universal support for the confinement of ionic liquid as an extraction medium, Separation and Purification Technology (2020) 117411. Q1, IF 7.278, DOI: 10.1016/j.seppur.2020.117411 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował analizę rozważanego tematu. Udział w korekcie Manuskryptu przed i po recenzji. Nadzorowałem prowadzone badania.*	15 %
3.	K. Delińska, P. W. Rakowska, **A. Kloskowski**, Porous material-based sorbent coatings in solid-phase microextraction technique: Recent trends and future perspectives, TrAC Trends in Analytical Chemistry (2021) 116386. Q1, IF 12.296, DOI: 10.1016/j.trac.2021.116386 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował analizę rozważanego tematu. Udział w korekcie Manuskryptu przed i po recenzji. Nadzorowałem pracę nad artykułem.*	20%
4.	K. Delińska, K. Yavir, **A. Kloskowski,** Head space for the analysis of organophosphorous insecticides by silica IL-based fibers in real samples, Molecules. Q1, IF 4.412, w recenzji. *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował konceptualizację badań eksperymentalnych, przeprowadziłem ocenę i analizę danych. Udział w korekcie Manuskryptu przed i po recenzji. Nadzorowałem prowadzone badania.*	15%
5.	K. Delińska, G. Machowski, **A. Kloskowski**, Development of SPME fiber coatings with tunable porosity for physical confinement of ionic liquids as an extraction media, Microchemical Journal (2022) 107392. Q2, IF 4.821, DOI: 10.1016/j.microc.2022.107392 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował konceptualizację badań eksperymentalnych, przeprowadziłem ocenę i analizę danych. Udział w korekcie Manuskryptu przed i po recenzji. Nadzorowałem prowadzone badania.*	20%

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Oświadczenie o udziale w publikacji

Lp.	Publikacja	Udział procentowy
1.	K. Delińska, **P. W. Rakowska**, A. Kloskowski, Porous material-based sorbent coatings in solid-phase microextraction technique: Recent trends and future perspectives, TrAC Trends in Analytical Chemistry (2021) 116386. Q1, IF 12.296, DOI: 10.1016/j.trac.2021.116386 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował analizę rozważanego tematu. Przygotowałam Rozdział I publikacji. Udział w korekcie manuskryptu przed i po recenzji.*	10 %

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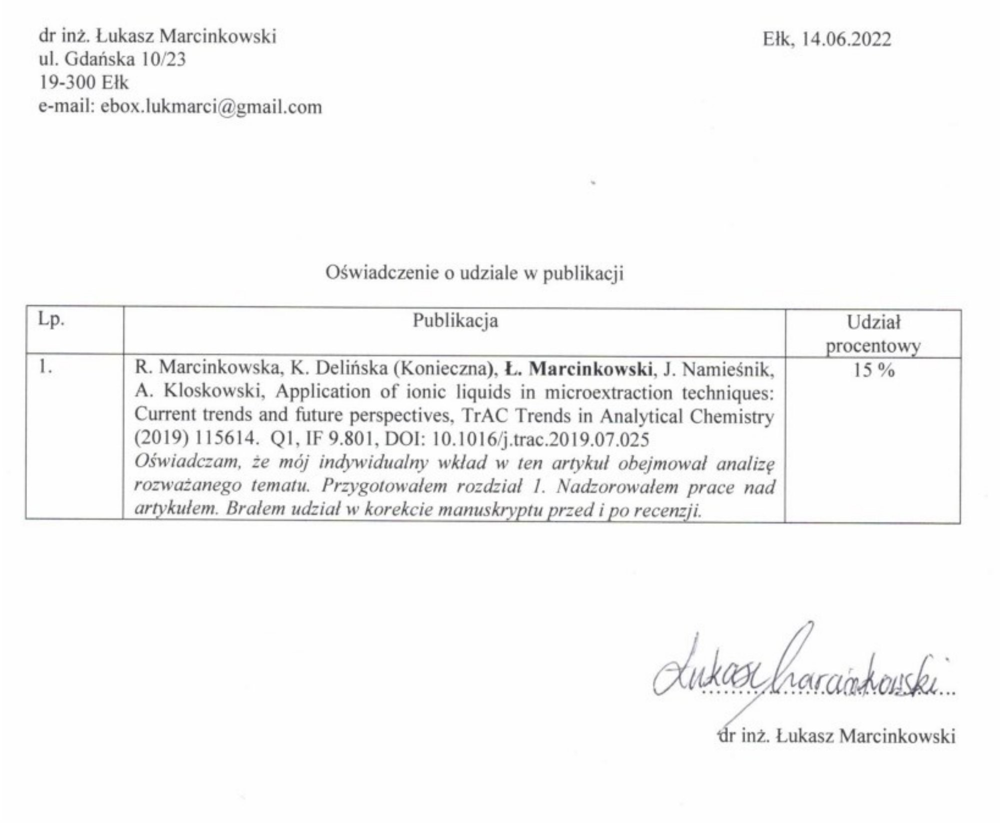

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Ełk, 14.06.2022

Oświadczenie o udziale w publikacji

Lp.	Publikacja	Udział procentowy
1.	R. Marcinkowska, K. Delińska (Konieczna), **Ł. Marcinkowski**, J. Namieśnik, A. Kloskowski, Application of ionic liquids in microextraction techniques: Current trends and future perspectives, TrAC Trends in Analytical Chemistry (2019) 115614. Q1, IF 9.801, DOI: 10.1016/j.trac.2019.07.025 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował analizę rozważanego tematu. Przygotowałem rozdział 1. Nadzorowałem prace nad artykułem. Brałem udział w korekcie manuskryptu przed i po recenzji.*	15 %

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Lp.	Publikacja	Udział procentowy
1.	K. Delińska (Konieczna), **K. Yavir**, M. Kermani, A. Mielewczyk-Gryń, A. Kloskowski, The new silica-based coated SPME fiber as universal support for the confinement of ionic liquid as an extraction medium, Separation and Purification Technology (2020) 117411. Q1, IF 7.278, DOI: 10.1016/j.seppur.2020.117411 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował analizę rozważanego tematu. Odpowiedzialność za wykonanie wybranych badań laboratoryjnych. Udział w korekcie Manuskryptu przed i po recenzji.*	20 %
4.	K. Delińska, **K. Yavir**, A. Kloskowski**,** Head space for the analysis of organophosphorous insecticides by silica IL-based fibers in real samples, Molecules. Q1, IF 4.412, w recenzji. *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował analizę rozważanego tematu. Udział w wykonaniu wybranych badań laboratoryjnych. Udział w korekcie Manuskryptu przed i po recenzji.*	15%

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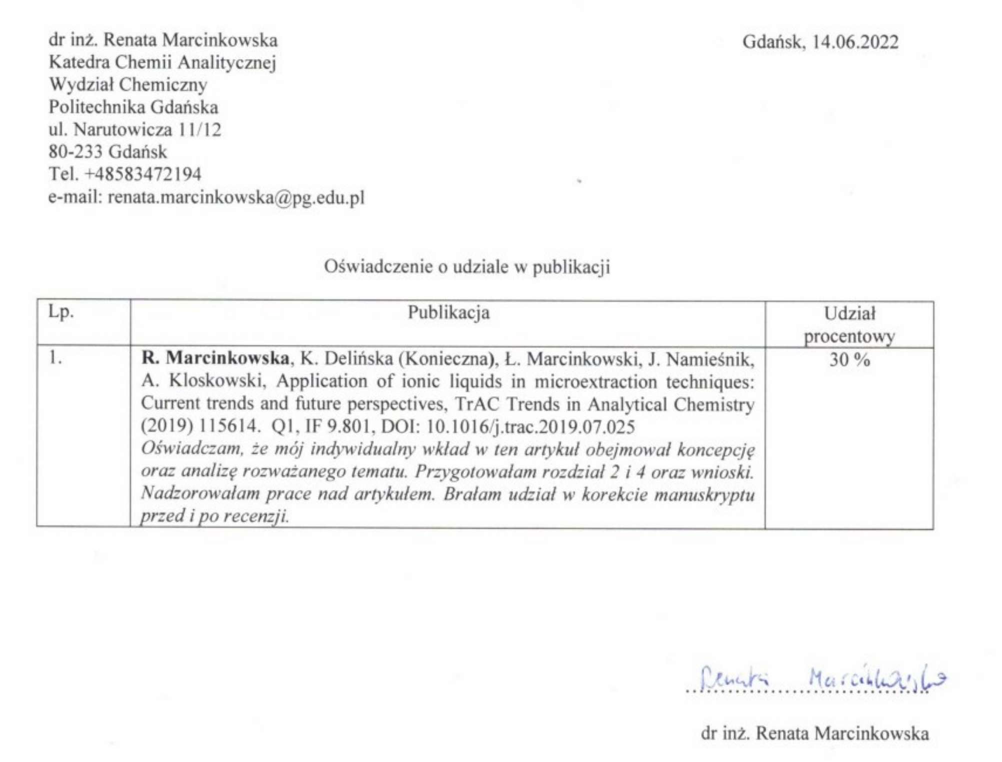

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Lp.	Publikacja	Udział procentowy
1.	**R. Marcinkowska**, K. Delińska (Konieczna), Ł. Marcinkowski, J. Namieśnik, A. Kloskowski, Application of ionic liquids in microextraction techniques: Current trends and future perspectives, TrAC Trends in Analytical Chemistry (2019) 115614. Q1, IF 9.801, DOI: 10.1016/j.trac.2019.07.025 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował koncepcję oraz analizę rozważanego tematu. Przygotowałam rozdział 2 i 4 oraz wnioski. Nadzorowałam prace nad artykułem. Brałam udział w korekcie manuskryptu przed i po recenzji.*	30 %

Renata Marcinkowska
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Lp.	Publikacja	Udział procentowy
1.	K. Delińska (Konieczna), K. Yavir, M. Kermani, **A. Mielewczyk-Gryń**, A. Kloskowski, The new silica-based coated SPME fiber as universal support for the confinement of ionic liquid as an extraction medium, Separation and Purification Technology (2020) 117411. Q1, IF 7.278, DOI: 10.1016/j.seppur.2020.117411 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował wykonanie badań oraz analizę wyników otrzymanych za pomocą Skaningowej Mikroskopii Elektronowej.*	10 %

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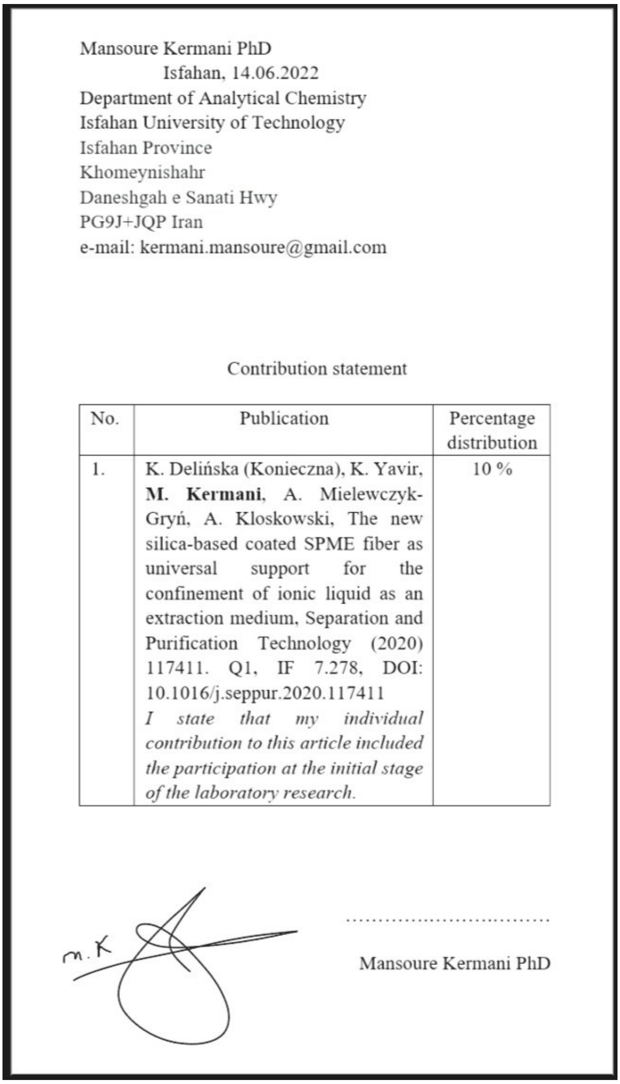

Mansoure Kermani PhD
Isfahan, 14.06.2022
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Contribution statement

No.	Publication	Percentage distribution
1.	K. Delińska (Konieczna), K. Yavir, **M. Kermani**, A. Mielewczyk-Gryń, A. Kloskowski, The new silica-based coated SPME fiber as universal support for the confinement of ionic liquid as an extraction medium, Separation and Purification Technology (2020) 117411. Q1, IF 7.278, DOI: 10.1016/j.seppur.2020.117411 *I state that my individual contribution to this article included the participation at the initial stage of the laboratory research.*	10 %

m.K

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Mansoure Kermani PhD

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Tel. +48126172430
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Kraków, 14.06.2022

Oświadczenie o udziale w publikacji

Lp.	Publikacja	Udział procentowy
1.	K. Delińska, **G. Machowski**, A. Kloskowski, Development of SPME fiber coatings with tunable porosity for physical confinement of ionic liquids as an extraction media, Microchemical Journal (2022) 107392. Q2, IF 4.821, DOI: 10.1016/j.microc.2022.107392 *Oświadczam, że mój indywidualny wkład w ten artykuł obejmował analizę i interpretację wyników uzyskanych metodą porozymetrii rtęciowej.*	10 %

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dr inż. Grzegorz Machowski

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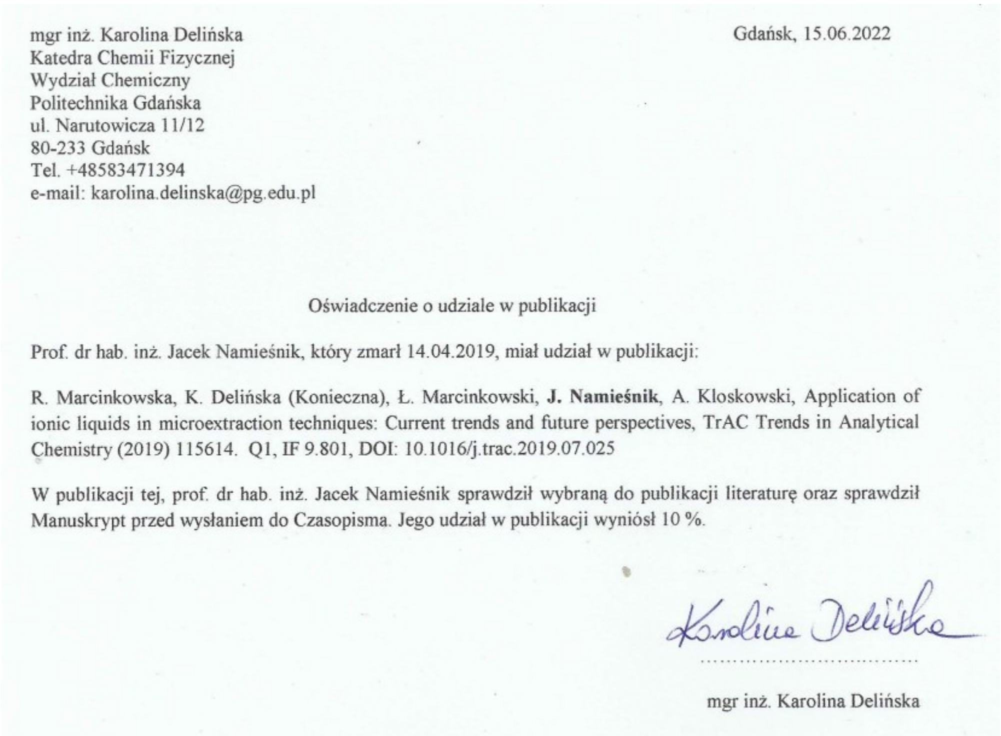

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Gdańsk, 15.06.2022

Oświadczenie o udziale w publikacji

Prof. dr hab. inż. Jacek Namieśnik, który zmarł 14.04.2019, miał udział w publikacji:

R. Marcinkowska, K. Delińska (Konieczna), Ł. Marcinkowski, **J. Namieśnik**, A. Kloskowski, Application of ionic liquids in microextraction techniques: Current trends and future perspectives, TrAC Trends in Analytical Chemistry (2019) 115614. Q1, IF 9.801, DOI: 10.1016/j.trac.2019.07.025

W publikacji tej, prof. dr hab. inż. Jacek Namieśnik sprawdził wybraną do publikacji literaturę oraz sprawdził Manuskrypt przed wysłaniem do Czasopisma. Jego udział w publikacji wyniósł 10 %.

Karolina Delińska
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mgr inż. Karolina Delińska

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