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Preparation of matrix-free reference materials of volatile analytes based on the controlled decomposition of surface compounds: a new concept♣

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The use of reference materials in analytical laboratories is on the increase. Undoubtedly, the reason for this is the need for traceable and therefore comparable results of measurements. The use of reference materials is necessary in all analytical laboratories and especially in those which examine environmental samples characterised by:

- low or very low concentration levels of analytes,
- complex matrices,
- temporal and spatial variability of samples, and
- the possibility of interference.

The development of analytical techniques for measuring components of gaseous media (outdoor air, indoor air, workplace air) has been going on for many years. This trend is closely associated with the need to obtain results of high quality, which necessitates the use of matrix-free (standard gaseous mixtures) as well as matrix reference materials. The use of reference materials with matrix compositions and analyte concentrations close to those of real samples yields more reliable measurement results.

This article presents a new approach to the problem of generating standard gaseous mixtures: the analyte is generated during the thermal decomposition of compounds immobilised on (i.e. chemically bonded to) the surface of an appropriate support material

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♣This article is dedicated to Professor Roman Leboda on the occasion of his 65th birthday

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1. INTRODUCTION

Since 1980s the European Commission (EC) has been supporting research programmes aimed at improving the quality of physical, biological and chemical measurements through the use of appropriate reference materials. The problems connected with their production and use in analytical practice, both in Europe and elsewhere, have been discussed at length. Figure 1 shows a general classification of reference materials [1-5].

In analytical chemistry, the significance of appropriate reference materials is increasing, especially in the context of:

- the validation of analytical methodologies;
- the calibration of control and measuring devices;
- the provision of measuring traceability;
- the estimation of the measurement result uncertainty.

The application of reference materials in analytical laboratories has increased considerably in recent years. This is unquestionably due to the necessity of obtaining traceable and therefore comparable results of analyses. Ensuring that analytical results are of the appropriate quality is an objective very difficult to achieve, but it is nonetheless essential, since false results of analytical tests can have adverse effects of a medical, economic and social nature.

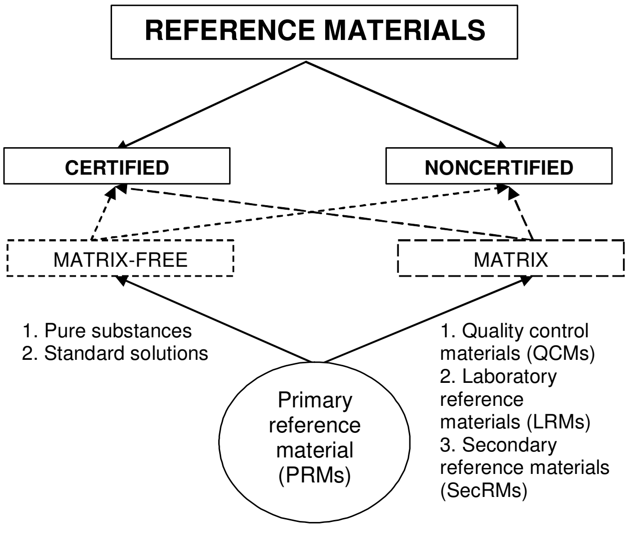


Fig. 1. Classification of reference materials used in chemical analysis [6, 7].

An important aspect of these considerations in the context of environmental protection is the improvement of the quality of air pollution measurements.

Investigations are carried out with the aim of identifying sources of errors in sampling and analysis, standardising methods, as well as conducting research into beneficial techniques of producing reference materials for gaseous constituents.

The reference materials for volatile analytes most often used in chemical analytics are:

■ **Standard gaseous mixtures obtained by known static techniques.** The final mixture is marketed in commercially available containers;

■ **Standard gaseous mixtures obtained by a dynamic technique.** In this case, suitable generators are commercially available for producing a stream of the component or components of the mixture to be measured in a stream of diluent gas;

■ **Sorption tubes** (filled with active carbon) containing the relevant quantity of organic analytes;

■ **Solutions of analytes in appropriate solvents.** This method is used for organic analytes of lower volatility.

It should be emphasised that only a small number of reference materials belonging to any one of the above groups are available. The application of these materials is not only fraught with technical difficulties but can also be a source of many errors, as a consequence of which the validation process may not fulfil its role in controlling and assuring the quality of analytical results.

The production of standards is an arduous, multi-stage process. The availability of reference materials for volatile compounds is limited; moreover, the magnitude of error, which affects the precision and accuracy of the final results of the analysis, depends closely on the stability and reliability of standard gaseous mixtures. As a consequence, new methodologies for producing them are continually being sought. We have therefore attempted to develop techniques for preparing standard gaseous mixtures with a very broad and regular range of concentrations of the component to be determined.

2. NEW CONCEPT FOR PREPARING MATRIX-FREE REFERENCE MATERIALS OF VOLATILE ANALYTES

This novel methodology for the production of standard gaseous mixtures involves the production of accurately determined quantities of analytes during the thermal decomposition of surface compounds. The approach utilises compounds immobilised on (i.e. chemically bonded to) the surface of a support material (silica gel, porous glass, glass rods coated with silica gel, glass fibres) which, under predetermined temperature conditions, undergo thermal decomposition or chemical rearrangement, thereby releasing a strictly defined quantity of volatile compound. The compounds released are purged from the reaction chamber (chromatograph injector, thermal desorber) by a stream of diluent gas to produce a stream of the standard gaseous mixture.

The support material for the surface compound plays an important part in this approach: which support material is selected will directly determine the quantity of the target analyte released. The perfect support material for surface compounds is characterised by [6]:

- Particles of uniform and/or spherical shape within a narrow range of dimensions;
- A uniform arrangement of active centres on the particle surface;
- A precisely defined porosity;
- High mechanical strength.

Samples of materials with a chemically modified surface can be treated as a convenient source of components (regarded as the classic example of matrix-free reference materials) only when the following requirements are fulfilled (Figure 2):

- The material is of the desired purity;
- The decomposition temperature of the surface compound is known;
- The degree of coverage of the surface of the support material by the surface compound is known;
- The degree of homogeneity of coverage of the surface of support material by the surface compound is known.

Figure 3 is a schematic diagram of the apparatus for generating standard gaseous mixtures by the thermal decomposition of immobilised compounds [7].

In order to generate a stream of a standard gaseous mixture using the apparatus shown in Figure 3, a glass tube containing a sample of the chemically modified material placed between two glass wool plugs is prepared. Silica gel, porous glass, or glass fibres of known length can be used as the support. Before use, the glass tubes should be silanised to minimise interactions between the container wall and the analyte. The tube and sample are placed in the chamber of a thermal desorber, previously heated to the desired temperature. The time required to heat the thermal desorber chamber depends on the kind of support used. After this time has elapsed, the four-way valve is switched to direct the gas mixture onto the head of the GC column, where it is sampled. After the sampling step, the four-way valve is returned to its original position.

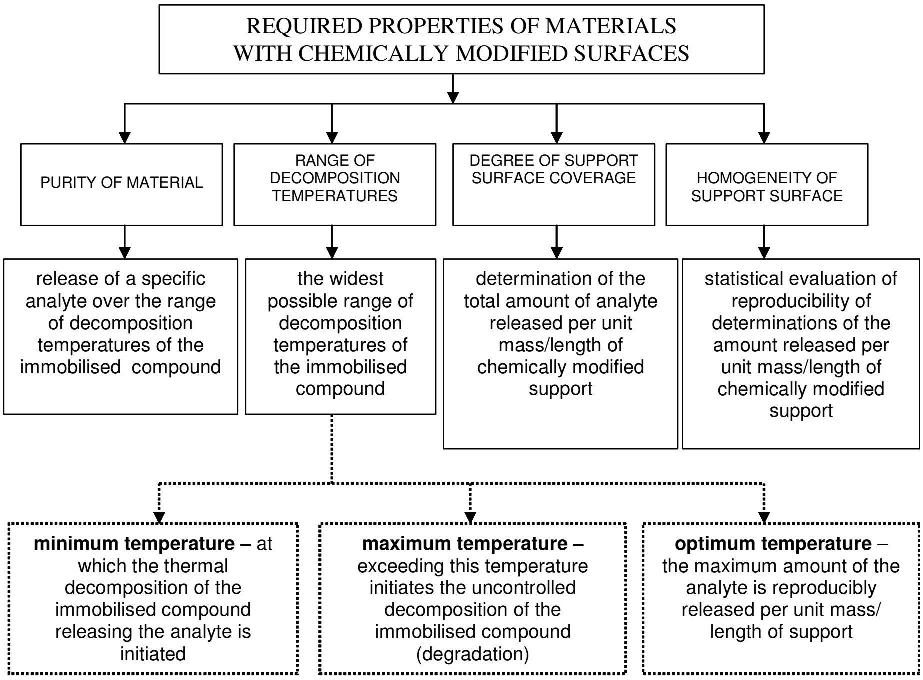


Fig. 2. The parameters used to evaluate the suitability of materials with chemically modified surfaces for the generation of standard gaseous mixtures [7].

The production of this type of reference materials is an arduous, multi-stage process. Since the magnitude of error, affecting precision and accuracy and hence the final results of the analysis, depends closely on the stability and homogeneity of standard materials, investigations of novel methodologies are increasingly focusing on the preparation of these materials. Our attempts to develop techniques for preparing gaseous standards with a very broad and adjustable range of concentrations of the component of interest are therefore a reflection of this trend (Tables 2, 3).

The development of techniques for preparing standard gaseous mixtures with a broad, adjustable and controlled range of analyte concentrations requires measuring devices that are less time- and labour-consuming.

Many different techniques for preparing standard gaseous mixtures are available, and selecting the right one for a particular purpose, i.e. one yielding a standard gaseous mixture with the desired operational parameters, depends on the nature of the analytes and diluent gas as well as on the required amount of analyte in the mixture. Other important parameters affecting the choice of method include the desired final volume of the standard gaseous mixture and the concentration(s) of analytes it is to contain.

Tab. 1. Characteristics of supports used for the preparation of immobilised compounds serving as a source of analytes for standard gaseous mixtures [8-19].

Type of support	Properties	Specific surface area [m^2/g]	Particle size [µm]	Pore size [nm]
Silica gel (MN-Kieselgel 60)	- Surface hydroxyl groups; - Readily available in different forms, varying with respect to particle shape and size, pore size and diversity, and specific surface area; - Favourable physical-chemical properties, such as: ● Mechanical resistance (it is not destroyed at pressures up to 65 MPa), ● Chemical inertness (over pH range 2 to 8), ● Thermal stability up to 250^{0}C, ● Possible replacement of silicon atoms with others, such as boron, magnesium or aluminium, ● Possible modification of both the surface and the geometric structure of pores (by hydrothermic processing or chemical binding of phases), ● High specific surface area and a large number of active sites per unit area => possible adsorption or binding of a larger quantity of compounds, - Highly homogeneous surface structure.	480–540	0.063–0.2	
Porous glass	- Possible manufacture of porous glass with specific properties (pore diameter, pore volume, specific surface area) and limited distribution of pores on the surface => the specific surface area is smaller than that of silica gel; - Sponge-like structure with SiO_2 groups => higher thermal stability and resistance to pH changes compared to silica gel; - Stronger adsorbing power than silica gel.	20–100	100–500	30–300
Glass fibres	- Coated with a thin film of stationary phase that can be used for extraction in SPME => direct introduction of a length of fibre into the heated injection chamber of the gas chromatograph => possible simplification of the thermal decomposition of the immobilised compound (generation of the desired amount of volatile component); - Elimination of the error related to sample weighing; - Specific surface area lower by three orders of magnitude than that of silica gel and porous glass.	fibre diameter 100 µm		

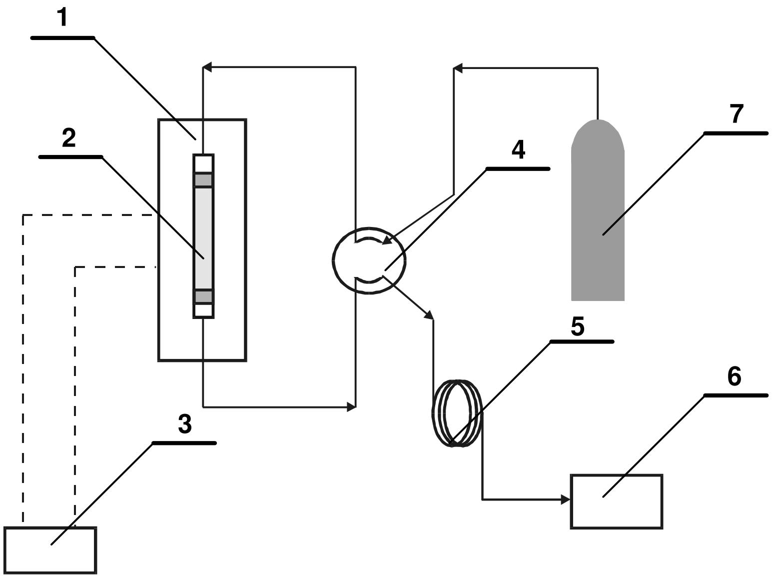


Fig. 3. Schematic diagram of the apparatus for generating standard gaseous mixtures by the thermal decomposition of immobilised compounds: 1– thermal desorber; 2 – glass tube containing the sample of the investigated material; 3 – temperature controller; 4 – four-way valve (chromatographic analysis); 5 – chromatographic column; 6 – detector; 7 – carrier gas tank [7].

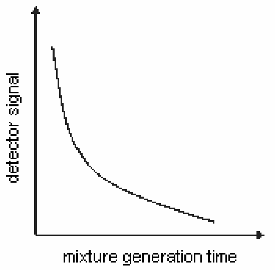
Tab. 2. Volatile analytes obtained by the thermal decomposition of an immobilised analyte.

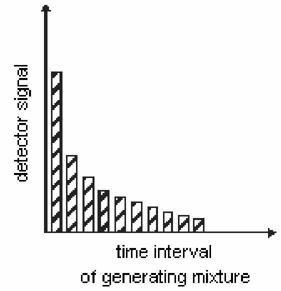
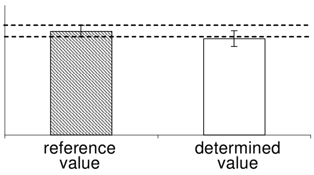
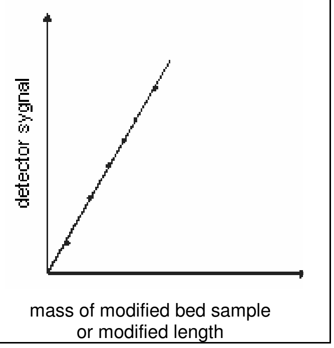
Type of support	Analytes	Amount of analyte	CV [%]	U (k=2) [%]	Reference(s)
Silica gel 35–70 mesh	CO_2	41 mg/g	2.7	2.9	[20]
Silica gel 35–70 mesh	CO	44 mg/g	3.1	3.4	[21]
Silica gel 35–70 mesh	CO CO_2	1.90 mg/g 2.70 mg/g	8.9 3.7	11 4.4	[20, 22]
Silica gel 35–70 mesh	C_2H_4	0.480 mg/g	3.0	3.1	[23]
Silica gel 35–70 mesh	CH_3Cl	3.40 mg/g	2.2	2.4	[24, 25]
Silica gel 35–70 mesh	NH_3	1.21 mg/g	1.7	1.9	[26]

Silica gel 35–70 mesh	CH_3NH_2	1.57 mg/g	1.9	2.0	[26]
Silica gel 35–70 mesh	$(C_2H_5)_2NH$	3.13 mg/g	0.94	1.1	[26]
Silica gel 35–70 mesh	$(C_2H_5)_3N$	4.04 mg/g	2.1	2.2	[26]
Silica gel 35–70 mesh	CH_2CHCH_2NCS	5.20 mg/g	2.4	2.7	[27]
Silica gel 35–70 mesh	C_4H_9NCS	6.50 mg/g	4.2	4.5	[27]
Silica gel 35–70 mesh	CH_3SH	13.2 mg/g	4.5	5.1	[28]
Silica gel 35–70 mesh	C_3H_7SH	17.4 mg/g	3.0	3.2	[28-30]
Silica gel 35–70 mesh	CH_3CHO	2.60 mg/g	4.8	5.0	[31]
Glass rods diameter 0.2 cm	CO	4.23 mg/cm	5.7	6.2	[32]
Glass rods diameter 0.2 cm	CO_2	15.0 mg/cm	5.2	6.1	[32]
Porous glass pore volume 1615 mm^3/g pore size 63 nm	C_2H_4	4.18 mg/g	0.87	0.95	[33]
Porous glass pore volume 1090 mm^3/g pore size 100 nm	C_2H_4	0.399 mg/g	2.9	3.2	[33]
Porous glass pore volume 940 mm^3/g pore size 126 nm	C_2H_4	0.390 mg/g	1.7	2.1	[33]
Porous glass pore volume 807 mm^3/g pore size 36 nm	C_2H_4	2.24 mg/g	1.4	1.6	[33]
Glass fibre covered with a layer of Al fibre diameter – 110 µm external diameter – 146 µm	C_2H_4	0.685 ng/cm	4.2	4.6	[34, 35]
Glass fibre covered with a layer of Al fibre diameter – 220 µm external diameter – 300 µm	C_2H_4	0.8300 ng/cm	0.81	0.98	[34]
Glass fibre covered with a layer of Al fibre diameter – 110 µm external diameter – 146 µm	C_2H_4	1.092 ng/cm	1.1	0.94	[34]
Glass fibre covered with a layer of Al thickness of metal layer – 50 nm	CH_3Cl	1.696 ng/cm	3.0	3.0	[36]

Glass fibre covered with a layer of Al thickness of metal layer – 100 nm	CH_3Cl	1.672 ng/cm	5.3	5.3	[36]
Glass fibre covered with a layer of Al thickness of metal layer – 200 nm	CH_3Cl	1.693 ng/cm	4.6	4.6	[36]
Glass fibre covered with a layer of Ti thickness of metal layer – 50 nm	CH_3Cl	1.678 ng/cm	3.9	3.5	[36]
Glass fibre covered with a layer of Ti thickness of metal layer – 100 nm	CH_3Cl	1.651 ng/cm	3.0	2.7	[36]
Glass fibre covered with a layer of Ti thickness of metal layer – 200 nm	CH_3Cl	1.663 ng/cm	3.3	2.8	[36]
Glass fibre fibre diameter – 100 µm	CH_3Cl	2.62 ng/cm	2.8	4.2	[37]

Tab. 3. Possible applications of the thermal decomposition of surface compounds.

Number of modified bed samples	Usage	Application	Graphic illustration
One sample	Heating in a stream of carrier gas, directing the standard mixtures onto the detector	Calibration – *on-line*	

One sample	Heating in a stream of carrier gas, directing the standard mixtures ('batchwise') onto the detector	Calibration – *off-line*, several points with one modified bed sample	
One sample	Heating in a stream of carrier gas, collection of analyte in a trap, directing the whole amount of the analyte to the detector	Validation – evaluation of accuracy	
Series of samples	Heating in a stream of carrier gas, collection of analyte in a trap, directing the whole amount of the analyte to the detector	Calibration – *off-line*, one point with one modified bed sample	

3. CONCLUSIONS

The thermal decomposition of surface compounds is a convenient way of producing standard gaseous mixtures, which are examples of matrix-free reference materials. This technique facilitates the relatively straightforward production of gaseous mixtures containing substances that are toxic, unstable or of disagreeable odour.

In addition to the way the support surface is modified, the composition of a standard mixture is also affected by the thermal decomposition parameters of a particular batch of modified support, such as:

- The amount (mass/length) of sample on the modified support;
- The thermal decomposition temperature of the immobilised compound;
- The flow rate of the diluent gas
- The duration of preparation of the standard gaseous mixture;
- The geometry and nature of the support for the immobilised compound.

Significant progress has been made recently in the development of techniques for preparing standard gaseous mixtures. This is partly due to the rapid development of new procedures for analysing indoor air pollutants at ever lower concentrations, requiring multicomponent standard gaseous mixtures. The growing demand for reference materials of this type has stimulated further research into the techniques of preparing standard gaseous mixtures containing ever smaller concentrations of analytes.

Another serious challenge is the production of new reference materials for volatile analytes in gaseous media, since at present there are just a few materials of this type commercially available.

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