Thermal Desorption Technical Support

Note 30: Certified Reference Materials for Analysis of VOCs in Air by Thermal Desorption (TD)/GC

Keywords

pre-concentrating, contaminants, certified analyte concentrations, uncertainty contribution

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Introduction

In environmental analytical chemistry, the analyst usually proceeds by pre-concentrating the contaminants extracted from a sample matrix, whether that matrix is water, waste, soil or gas. Bias in a method is a typically estimated by analysing a representative or control sample of the matrix loaded with known amounts of the contaminant. Estimating bias is uniquely difficult if the matrix is workplace or ambient air.

Simple adherence to a written standard, (such as MDHS 80[1], ISO 16017[2], ASTM 6196-3[3], US EPA Method TO-17[4]), does not guarantee a satisfactory performance. It is essential that operators of these procedures are fully qualified and trained. The use of certified reference materials (CRMs) is a check on the calibration of the method (the usual source of errors) and quality control. However it is not a substitute for training.
Other checks on the procedure are participation in external QA schemes such as WASP[5] (Workplace Scheme for Analysis and Sampling Proficiency). This paper relates to the use of reference materials for the analysis of VOCs in air by thermal desorption (TD) GC.

The analysis of VOCs in air by thermal desorption

Air standards may take various forms. Certified reference cylinders of compressed gas mixtures are available but their traceable preparation and certification can only be undertaken by a few centres of excellence. Even then, their certificates are valid only for the compressed contents. Without scrupulous precautions, losses can occur when gas samples are taken through pressure regulators and the total volume sampled has to be traceable to some primary standard.

Lower pressure canister standards are similarly difficult to prepare with certified analyte concentrations thus making them very expensive. Although they do not suffer to the same extent as pressurised cylinders with regard to potential losses in pneumatic control components, the volume of standard gas contained in a typical canister and thus the lifetime of the standard is limited.

Air samples which are to have their vapour phase organic content analysed by thermal desorption (-GC or -GC/MS) are typically passed through a sorbent cartridge or tube during the sampling process and are collected at the microgram or nanogram level. A CRM intended for thermal desorption of an air sample may therefore be prepared on a sorbent tube and desorbed/analysed in exactly to the same way as a sample tube. According to guidelines issued by the Commission of the European Communities, Community Bureau of Reference (European BCR), a reference material may be certified on the basis of preparation, provided that traceability is achieved to the primary standard(s) to which the units of the certified properties refer. The typical BCR certification procedure was based on laboratory comparisons either using independent methods or by analysis under reproducibility conditions, to which a minimum of 6 laboratories participated and this makes a CRM overly expensive.

CRMs are therefore too costly for use as routine calibration standards. Their utility lies in testing the whole analytical process, including calibration. Given the expense and length of time it takes to complete the necessary storage validation tests and laboratory analytical intercomparisons, only two thermal desorption CRMs have ever been made available namely, mainly CRM 112 (benzene, toluene, *m*-xylene on Tenax TA) and CRM 555[7] (dichloromethane, 1,1,1-trichloroethane, trichloroethane, tetrachloroethane, toluene on Tenax GR). They consist of standard steel tubes, 89 mm x ¼-inch O.D., sealed with ¼-inch brass Swagelok-type caps and combined PTFE ferrules. CRM 112 and CRM 555 are available from all distributors of European BCR materials. Certified Reference Standards (CRS), prepared by an institute authorised to issue appropriate certificates, (*i.e.* a standards laboratory or an accredited calibration laboratory) are now commercially available for routine in-house quality control of thermal desorption procedures. These are significantly lower cost than CRMs and are typically prepared either by (1) flow-controlled introduction of a known volume of standard atmosphere (according to ISO 6145 (1981) part 8) or (2) syringe introduction of liquid standards (traceable by gravimetric methods). Both standard preparation methods are capable of minimal bias and have been used to certify CRMs. **Note: only standard atmospheres generated via permeation/diffusion cells have actually been used to prepare primary CRMs.** Those factors contributing to the overall uncertainty of analyte masses in the standards have also been well characterised and quantified for both preparation methods.

The preparation of Certified Reference Standards from standard atmospheres

Sampling a known volume of standard atmosphere containing the compounds of interest has the inherent advantage that the standard is prepared using a method that is directly analogous to the actual air sampling process.

As such this methodology, applying dynamically generated standard atmospheres, has been used for the preparation of the BCR 112, 555 and is the first choice in the current ISO standards (*e.g.* ISO 16017) for the measurement of volatile organic compounds in ambient, indoor and workplace air[6]. It is the only methodology of choice in case of incompatibility of analysis with solvents used in liquid spiking.

Preparation of sorbent tube standards from dynamic standard atmospheres is essentially a three-step process:

1. Delivery and control of known mass flows of the compounds of interest
2. Addition and mixing of a known flow of purified air
3. Collection of a known volume of the standard atmosphere prepared in steps 1 and 2 on a conditioned standard tube.

A typical system for this purpose is shown in Figure 1.

For the delivery and control of compound mass flows various techniques such as injection, dynamic blending from cylinder standards, permeation and diffusion may all be used. Each of these methods has its own range of application.

The uncertainty in the momentary delivery rate (*N.B.* some of these effects may be levelled off in longer-term experiments) is largely determined by the following contributors:

- the purity of the compounds delivered
- the determination of the mass flow
- effects of temperature and pressure variations

The effect of the purity of the compound is commonly overlooked. However, the use of a compound of 95% purity will introduce an an

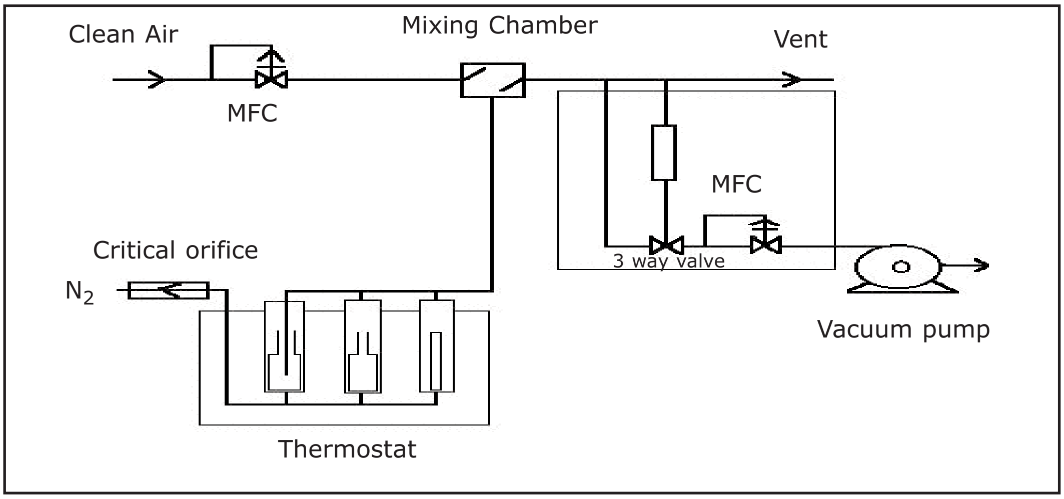

Figure 1: Schematic of preparation of sorbent tube standards from dynamic standard atmospheres

immediate uncertainty of 1.4% in the final concentration. For compounds with purities >99%, the contribution of the uncertainty of the purity is generally negligible (<0.3%).

Mass flows are usually measured by continuous or periodic weighing. By applications of high resolution weighing equipment (10 µg resolution) and by using appropriate weighing intervals, the mass flow may be measured with a relatively low uncertainty (*e.g.* approximately 0.25% for a flow of 0.5 µg/min with four-weekly weighings).

The actual temperature and pressure may affect the delivery rate of permeation and diffusion cells, the viscosity and specific mass of injected liquids and the flow of gas from a cylinder standard.

For example, the delivery rate of permeation cells may vary by as much as 10% per degree Kelvin (°K), giving an uncertainty contribution of 2.5% for a temperature controlled to within ±0.25 K (Note that this is a reasonable objective as the temperature of permeation cells is mostly determined by the temperature of the purge gas used).

In the dilution step, mass flow controllers (MFC) are used to deliver and control the volume flow rate of the dilution air. By using multiple purification steps, typical air constituents may be removed to sub-ppb concentration levels. The purification and control of diluent air is of crucial importance when generating standard atmospheres in the low- and sub-ppb range (*e.g.* a background level of <1 ppb of a compound contributes to uncertainty of 3% at the 10 ppb level).

Mass flow controller calibration and/or actual air volume flow measurement is typically performed using high-precision flow meters such as electronic piston provers or soap bubble meters. By application of corrections for differences between temperatures and pressures at the time of calibration and at the actual time of application, allowing for mass-flow controller variability, an uncertainty in the actual flow rate of 0.3% may be achieved when calibrating the air flow rate before each experiment.

In a more practical situation, using less accurate flow meters without appropriate corrections, the uncertainty may amount to several %.

Similar considerations must go for the flow rate measurement in the process of sampling from a standard atmosphere. By application of suitable timing systems, the uncertainty contribution of the sampling time to the sampling volume can be kept to a negligible level (approximately 0.02%).

Factors not to be overlooked are the minimum and maximum allowable sampling volumes. A low sample volume may contribute considerably to the sampling uncertainty due to dead volumes present in the sampling manifold. On the other hand, too large sample volumes my lead to compound losses due to sorbent tube breakthrough.

In table 1, an overview is given of estimated uncertainty contributions under conditions of

Uncertainty Factor	**Best Available (%)**	**Practical (%)**
Mass flow of compound		
compound purity	<0.3	<0.3
weighing	0.25	2.5
short-term variations	0.5	2.5
Dilution air flow		
purity	0.3	3
flow calibration	0.3	2.6
short-term variations	0.2	0.2
Sample volume		
flow calibration	0.3	2.6
timing	0.05	1
TOTAL UNCERTAINTY	**0.9**	**6.0**

Table 1: Uncertainty contributions of various factors to the preparation of a benzene calibration tube standard

full control using best-available techniques, and for conditions estimated to be more practical in the real world. In the table, the example of sampling from a benzene standard atmosphere of 10 ppbv [approximately 32.5 µg/m^3 at 293 K (approximately 20°C) and 101.3 kPa (approximately 1 atmosphere)] with a mass flow of 0.5 µg/min has been used. In the case of the best available techniques a diffusion cell was used whereas in the practical application a permeation cell was used.

Preparing standards *via* liquid spiking

Given its inherent simplicity, most routine thermal desorption calibration standards and some CRS tubes are prepared using syringe injection of liquid standards. Its use is described (briefly) in various MDHS methods as well as in NIOSH 2549 and US EPA Method TO-17. Typically 10-100 mg analyte is injected into 5-25 ml solvent in a septum-sealed flask to make a stock solution. This is then diluted, using normal laboratory procedures, to make standard solutions of appropriate concentrations *i.e.* such that an injection of 1-5 µl contains a mass of analyte representative of that sampled under typical monitoring conditions. **Note that this can range from low ng levels for ambient atmospheric monitoring to high microgram levels for some workplace air applications.** Liquid standard is typically introduced onto the conditioned sorbent tube using a calibrated microsyringe and some type of sealed, preferably unheated injection port *i.e.* by injecting a few microlitres of liquid standard onto the sampling end of the tube via the injection port, whilst the port and tube are purged with a stream of pure gas (A commercially available Calibration Solution Loading Rig (CSLR) which meets the criteria laid down in the above methods is available from Markes International Ltd. part number C-CSLR). If it is convenient/possible to prepare the standard in a solvent which is unretained by the sorbent in the sample tube, the tube can be left attached to the injection port with the gas flowing until all solvent vapours have been purged from the sorbent.

Minimising errors (bias) in the preparation of sorbent tube standards by liquid spiking

In the generation of CRS tubes *via* liquid spiking, every step should be traceable to a primary standard. The critical step, and the one least discussed, is the calibration of the microlitre syringe. Dispensing 1-5 µl of volatile solvents is outside the scope of standards like BS7653 (piston and/or plunger operated volumetric apparatus). The manufacturer may certify the engineering standard of the syringe if requested, but at the microlitre level this certificate may not reflect the volume accurately delivered. Calibration must be done under the same conditions as those used to spike the sorbent tubes, *i.e.* if the tubes are spiked through the septum, the syringe calibration must involve penetration of a septum. If the solvent is methanol, the syringe must be calibrated with methanol, or at least a liquid with similar characteristics and certainly not water or mercury. HSL calibrates 5 µl syringes by repeatedly injecting methanol (d20=0.791) or bromoform (d20=2.88) into small septum-sealed vials and recording weight differences with an uncertainty of not greater than ±1%.
There is evidence that penetration of the septum may remove 50-100 nl of liquid from the needle.

Table 2 shows a comparison of the calibration of a 5 µl syringe (SGE 5A-FN-GP) with mercury, bromoform and methanol carried out by HSL.

Calibrant	Mean volume (µl) (n=6)	Std. error of mean
mercury: open vial	5.001	0.002
bromoform: open vial	5.00	0.01
bromoform + septum	4.91	0.02
methanol + septum	4.89	0.02

Table 2: Syringe calibration showing the effect of septum penetration on the delivery volume of SGE model 5A-FN-GP

The syringe was equipped with a repeating dispenser and preset to a nominal volume of 5.00 ± 0.02 µl.

Note that the mercury calibration shows the high engineering standard of manufacture, but is not an indicator of performance in practice.The effect with and without septum penetration is noticeable with an involatile liquid like bromoform, although difficult to demonstrate with methanol.

Injections onto the sorbent tube may be made with ‘hot needle’ or ‘cold needle’. On balance cold injections are preferred, though some might favour hot injections if the syringe is of the ‘plunger in needle’ type. In the conventional 5-10 µl syringe, some of the needle content evaporates in a hot injection, contributing an additional 1-2% to the total volume. The repeatability is also slightly degraded. Table 3 shows a comparison of cold and hot spiking of hydrocarbons in methanol (carried out by HSL).

Note that a ratio of 1.018 for toluene means that 15% of the toluene in the needle dead-volume was vaporised in the hot-needle injection.
The practicality of purging solvent from the standard tube before analysis varies according to the application. There is a risk of preferential loss of more volatile components by a ‘wash-out’ effect as very high concentrations of solvent vapour permeate the sorbent bed (Note that this problem is made worse if all or part of the standard is allowed to reach the sorbent bed without vaporising, *i.e.* in liquid form). Conversely, if a relatively large concentration solvent is left in the tube, its presence could affect the split-ratio or interfere with the analysis chromatographically. In each case, tests with and without solvent purge should be carried out to establish the effect on chromatography, analyte recovery, split-ratio, internal standard *etc*. In the above example methanol was removed from Tenax with 200 ml nitrogen at 50 ml/min before analysis. For more volatile analytes, a methanol solvent/Tenax TA adsorbent combination is not always advisable. For example acetone, hexane, dichloromethane and 1,1,1-trichloroethane are all lost from Tenax to some extent during a liquid spiking procedure. Chromosorb 106 can be substituted as the

Hydrocarbon	hot needle (n=12)		cold needle (n=6)		hot:cold
(~10 µg/5 µl)	**mean ± S.D.**	**% R.S.D.**	**mean ± S.D.**	**% R.S.D.**	
toluene	713.3 ± 7.3	1.2	700.7 ± 6.9	1.0	1.018
m-xylene	714.8 ± 6.4	0.9	709.9 ± 3.7	0.5	1.007
1,2,3-trimethyl benzene	655.7 ± 5.6	0.9	649.9 ± 1.8	0.3	1.009
n-undecane	564.6 ± 4.9	0.9	558.6 ± 1.7	0.3	1.010

Table 3: Comparison of hot- and cold-needle spiking of hydrocarbons in methanol solution on a standard 89 mm x 1/4-inch O.D. stainless steel tube packed with 150 mg Tenax TA using SGE syringe model 5A-FN-GP (Area counts x 10^{-3})

sorbent, although in this case methanol cannot be eliminated completely - about 0.05% remains when 250 mg Chromosorb 106 tube is purged with 1000 ml carrier gas. This does not usually interfere with the chromatographic analysis unless the GC split-ratio is very small. Chromosorb 106 is the best sorbent for preparing temporary calibration standards of such compounds, but as a CRM substrate, it does have some disadvantages relative to Tenax - its blank background is higher, residual solvent is undesirable and some chloroalkanes are not stable for storage periods longer than 6 months.

Comparing Methods of standard preparation

Discrimination tests have been carried out by loading sorbent tubes *via* liquid spiking and comparing the data with those obtained from tubes prepared from gas standards generated by motorised syringe/vapourising injector techniques (Table 4). Toluene was used as the internal standard reference. These tests demonstrated that on Chromosorb 106 the was no intrinsic difference between the two techniques for the chloroalkanes 1,1,1-trichloroethane, trichloroethane and tetrachloroethane.

	Gas generated (1 L; 0.5 ppm)	Liquid spiking (5 µl methanol /2 µg analyte)
1,1,1-trichloroethane	0.207	0.207
trichloroethane	0.199	0.200
tetrachloroethane	0.174	0.174

Table 4: Flame detector response factors of chloroalkanes, relative to toluene- comparing two methods of charging 250 mg Chromosorb

Summary

To summarise, certified reference standard (CRS) tubes containing sorbent preloaded with ng to µg levels of specific organic compounds can be generated from primary standards using either of the approaches described. Being lower cost than Certified Reference Materials they provide a convenient tool for in-house quality assurance of the complete TD-GC(-MS) analytical process and associated calibration protocols. Routine use of CRS tubes complies with guidance given in international standards and provides continual assurance of system and procedure reliability thus contributing to staff confidence. In these respects, in-house use of CRS tubes complements participation in external validation schemes such as WASP.

References

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2. International Standards Organisation, *ISO 16017 Air quality - Sampling and analysis of volatile organic compounds in ambient air, indoor air and workplace air by sorbent tube/thermal desorption/capillary gas chromatography. Part 1: Pumped sampling, Part 2: Diffusive sampling*

3. The American Society for Testing and Materials, ASTM D6196-03 *Standard practice for selection of sorbents, sampling and thermal desorption analysis procedures for volatile organic compounds in air.*

4 United States Environmental Protection Agency (US EPA) Method TO-17 *Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes.*

5. The Workplace Analysis Scheme for Proficiency (WASP), coordinated by the UK Health and Safety Executive.

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