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Soil quality — Guidelines for the identification of target compounds by gas chromatography and mass spectrometry

Qualité du sol — Lignes directrices pour l'identification des composés cibles par chromatographie en phase gazeuse et spectrométrie de masse

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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Introduction

In many analytical standards, use is made of gas chromatography (GC) in combination with mass spectrometric (MS) detection. This detector is a powerful tool provided it is properly used. In this International Standard, guidelines are given for the identification of target compounds. This International Standard can be used in combination with specific analytical standards or in combination with any GC-MS procedure. The result of the procedure described is: identified, indicated or absent.

Soil quality — Guidelines for the identification of target compounds by gas chromatography and mass spectrometry

1 Scope

This International Standard gives criteria for gas chromatography and mass spectrometry (GC-MS) identification of target compounds in soil samples. This International Standard is intended for use with standards developed for the determination of specific compounds. The identification criteria are based on the comparison of retention times followed by interpretation of the electron ionization mass spectra, or if necessary, additional mass spectrometric techniques and other relevant factors.

NOTE This International Standard is also applicable for other environmental samples.

2 Principle

A target compound is identified if the measured values meet the criteria specified in this International Standard or in the standard in which the procedures are described to analyse the target compound. Criteria are based on the relative retention times and the intensity of diagnostics ions selected in the scan mode and measured in the selected ion mode (SIM), and other relevant factors. Additional information regarding diagnostic ions from specific international standards on the analysis of the target compound can be used. The principle of identification points is used.

3 Terms and definitions

For the purpose of this document, the following terms and definitions apply.

3.1
target compound
selected component, the presence or absence of which is being established

NOTE This definition also applies to derivatives of the original compound which are formed during an intentional derivatization procedure or on-line derivatization.

3.2
standard compound
target compound with the highest possible purity, which can be used as a reference during the analysis

NOTE Any impurities should not have any influence on the mass spectrum of the standard compound.

3.3
retention time standard
compound that is added to the sample (or to the sample extract) and to the calibration standard solution, and used to calculate the relative retention times of the target compounds

NOTE The retention time standard may be identical to the internal standard(s).

3.4
relative retention time
ratio between the retention time of the target compound and the retention time of the retention time standard

3.5
lowest concentration for identification
lowest concentration of the target compound, which, if present in the sample, can be identified using the identification criteria in this International Standard

NOTE 1 It requires that the selected diagnostic ion with the lowest intensity is still present in the mass spectrum with a signal to noise ratio (S/N) higher than 3:1.

NOTE 2 This concentration is very dependent on the sensitivity of the instrument and on the performance characteristics of the analytical method.

3.6
diagnostic ion
selected fragment ion, molecular ion or other characteristic ion from the mass spectrum of the target compound with the highest possible specificity

3.7
identification point
result of mass spectrometric investigation or other investigations/information to identify a component in environmental matrices

3.8
selected ion mode
SIM
measuring the intensity of selected diagnostic ions only

4 Apparatus

As this International Standard is complementary to other standards using GC-MS, it is assumed that the instrumentation used meets the requirements of those standards and a detailed description is not within the scope of this International Standard. Suitable quality assurance requirements are set out in ISO/IEC 17025.

Minimum requirements are:

Ionization mode:	Electron ionization.
Electron energy:	Depending on the application (usually 70 eV).
Mass range:	Peaks (masses) with a S/N < 3 are not taken into consideration and the scan range is limited to 35 (to avoid the measurement of oxygen and nitrogen) to the highest mass of the target compound + 10 unified atomic mass units (u) in full scan measurements.
Scan rate:	The scan rate should be 10 times the peak frequency with a minimum of 7 scans per peak.
Scan mode:	Cyclic, linear.
	Full scan or selected ion monitoring.
Mass resolution:	To be tuned on nominal resolution, the peak width at half-height of every tune mass should not exceed 0,7 u.

5 Procedure

5.1 Retention times

The relative retention time of the target compound shall be determined using a calibration standard solution containing an appropriate number of internal standards. The use of internal standards is often prescribed in the specific standard describing the determination of the target compound. The relative retention times are calculated using the retention time standard(s). The calculated relative retention time shall have a value below 2.

5.2 Mass spectra, selection of diagnostic ions

If available, three diagnostic ions shall be selected for each target compound. Their intensities I_1, I_2, I_3 shall be determined in the calibration standard solution (at least three injections) as the peak area or peak height of the corresponding extracted ion current chromatograms. The relative intensities are calculated as the ratio of the determined peak heights (or areas) and the peak height (or area) of the most intensive diagnostic ion. Annex A gives a table of suitable diagnostic ions for a range of substances. Diagnostic ions may also be specified in the standard method being used.

It is not always possible to obtain three diagnostic ions (for instance, polycyclic aromatic hydrocarbons). In that case, select the available ions.

Diagnostic ions should have a high "uniqueness value" [3]. It is suggested that:

— high *m/z* values should be preferred due to their higher significance;

— even mass fragments are preferred over odd ones;

— if possible, the molecular ion should be selected as one of the diagnostic ions;

— the intensity of diagnostic ions is preferably higher than 15 % in relation to the base peak in the spectrum;

— if characteristic isotope clusters are present in the mass spectrum (e.g. chlorine), two diagnostic ions should be selected from one isotope cluster. Isotopes can be very characteristic for complex compounds, i.e. organotin;

— if during the sample preparation, the target compounds have been derivatized with a reagent with low specificity, only one of the ions M^+ and $[M\text{-der}]^+$ should be selected as a diagnostic ion (M^+ is the molecular ion of the derivatized target compound);

— in the selection of the diagnostic ions, possible column artefacts have to be taken into consideration, avoiding corresponding masses (e.g. *m/z* 73, 207, 281);

The peak shape and retention time of all measured diagnostic ions shall be identical. Co-eluting substances may influence the peak shape. As long as the peak of interest can be separately integrated, it may be used. Criteria for the retention time are the peak maxima of the extracted ion current chromatograms.

Diagnostic ions are supposed to originate from the analyte under investigation only. This implies that theoretically all diagnostic ions belonging to one and the same analyte have the same retention time. If the retention time of one selected diagnostic ion differs from the retention times of the other diagnostic ions from the same analyte, a co-eluting substance or a partly-separated substance giving the same mass may be present. In this case, the particular diagnostic ion cannot be used.

The accuracy of the retention time depends on the number of scans within the chromatographic peak and hence, on the scan rate. Because the scan rate is limited, small differences in the retention times of the diagnostic ions should be allowed.

A suitable criterion for the allowed difference in retention times of all diagnostic ions of an analyte shall not be greater than 20 % of the peak width at half the peak height. Therefore, the differences in retention times of the peak maxima of all the selected diagnostic ions in the extracted ion current chromatograms belonging to the same analyte shall not be greater than 20 % of the peak width at half the peak height. For most analyses, this means an acceptable difference of 1 s. These criteria apply for both the calibration standard solution and the sample.

NOTE 1 MTBE and TAME have *m/z* 73 as diagnostic ion.

NOTE 2 Due to overloading, the ratios of the diagnostic ions can change.

6 Qualification

6.1 GC-MS procedure

The procedure to qualify a component consists of three steps (see the flow scheme in Figure 1).

— **Step 1**: Gas-chromatographic result

The relative retention time shall fulfil the specified criteria (see 6.3, Step 1). Only if Step 1 is positive, can Step 2 be made.

— **Step 2**: Gathering identification points using analytical procedures

For qualification, the principle of identification points is used [1]. Identification points can be obtained from mass spectrometric data, but also using other analytical information.

— **Step 3**: Gathering additional identification points using knowledge and interpretation of this knowledge about the sample or sampling site.

Then the following classification can be obtained.

a) *Identification* (see 6.3.1)

The target compound is present in the analysed extract. At least three identification points are obtained.

b) *Indication* (see 6.3.2)

The target compound may be present. One or two identification points are obtained.

c) *Absence* (below the detection limit) (see 6.3.3)

No identification points are obtained using mass spectrometry.

First, the mass spectrometric results are evaluated. For every ion peak meeting the criteria given in 6.3, Step 2, an identification point is obtained. Three identification points give a positive identification. If less then three ion peaks are available [due to sensitivity (S/N < 3) or absence of fragments (PAH)], additional identification points shall be gathered using additional evidence. Possibilities are given in Table 1 and also explained in Annex B.

Table 1 — Examples of number of identification points, provided criteria are met

Source	Identification points *n*	Remark
Diagnostic ion	1	Every ion S/N > 3
Absence of any other ions in full scan	1	Diagnostic ions in full scan S/N > 3
Column with other polarity [a]	1	GC-criterion (extra retention time value)
Isotope dilution	1	
Component spike/standard addition	1	
Chromatographic pattern	1	i.e. PCB, PAH, dioxins
Other analytical techniques	1	Every other selective detector (i.e. ECD) or technique (i.e. LC)
GC-MS (EI and CI; positive/negative)	3	1 (EI) + 2 (CI)
GC-MS-MS	4	1 precursor and 2 daughters (product ion)
HR-MS (high resolution MS)	2	Every ion S/N > 3
Expectation, plausibility, earlier investigations	1	See 6.2
NOTE More examples with different techniques are found in Reference [1].		
[a] Not valid for non-separated compounds (isomers) with the same mass (chrysene/triphenylene, *m/p*-xylene).		

6.2 Additional information

Interpretation of environmental data is always a combination of data analyses, knowledge about the origin of the sample, knowledge on the behaviour of contaminants and processes that occur or may occur. This is also true for the interpretation of GC-MS analysis. As stated, a component is identified if 3 identification points are obtained. If only 1 or 2 diagnostic ions are present, additional identification points are necessary. In this International Standard, gathering additional identification points using analytical procedures is part of Step 2. Using information about the sample, and interpretation of this information, takes place in Step 3. An extra identification point is obtained if one or more of the following criteria is fulfilled.

NOTE Strictly taken, an identification point obtained in Step 3 is of another order than the identification points obtained in Step 1 and Step 2. They are obtained by interpretation of additional non-analytical information. In this International Standard, the term "identification point" (3.7) is used for the points obtained in all three steps.

Step 2: Gathering identification points using analytical procedures.

— No other ions are visible in full scan mode and this is in agreement with the mass spectrum of the pure component (for instance, PAH).

— Identification is in agreement with the chromatographic pattern normally present or present on that site (for instance, PCB or PAH).

— For volatile compounds, the specificity of the mass fragments in combination with their retention time will generally be sufficient. Their volatility corresponds to a low molecular mass, limiting the number of possible false positive results: there are no low molecular mass compounds with the same retention time on a GC column and also having similar mass spectra.

Step 3: Gathering additional identification points using knowledge and interpretation of this knowledge about the sample or sampling site. If identification points are obtained using Step 3, this shall be reported.

— The component is identified in earlier samples from the same site (for instance, if the sample under investigation has a low concentration and one or two diagnostic ions have S/N < 3 following the biodegradation.

— From historical investigation, it was shown that presence of the component was expected.

— Other samples from the same site give positive identification.