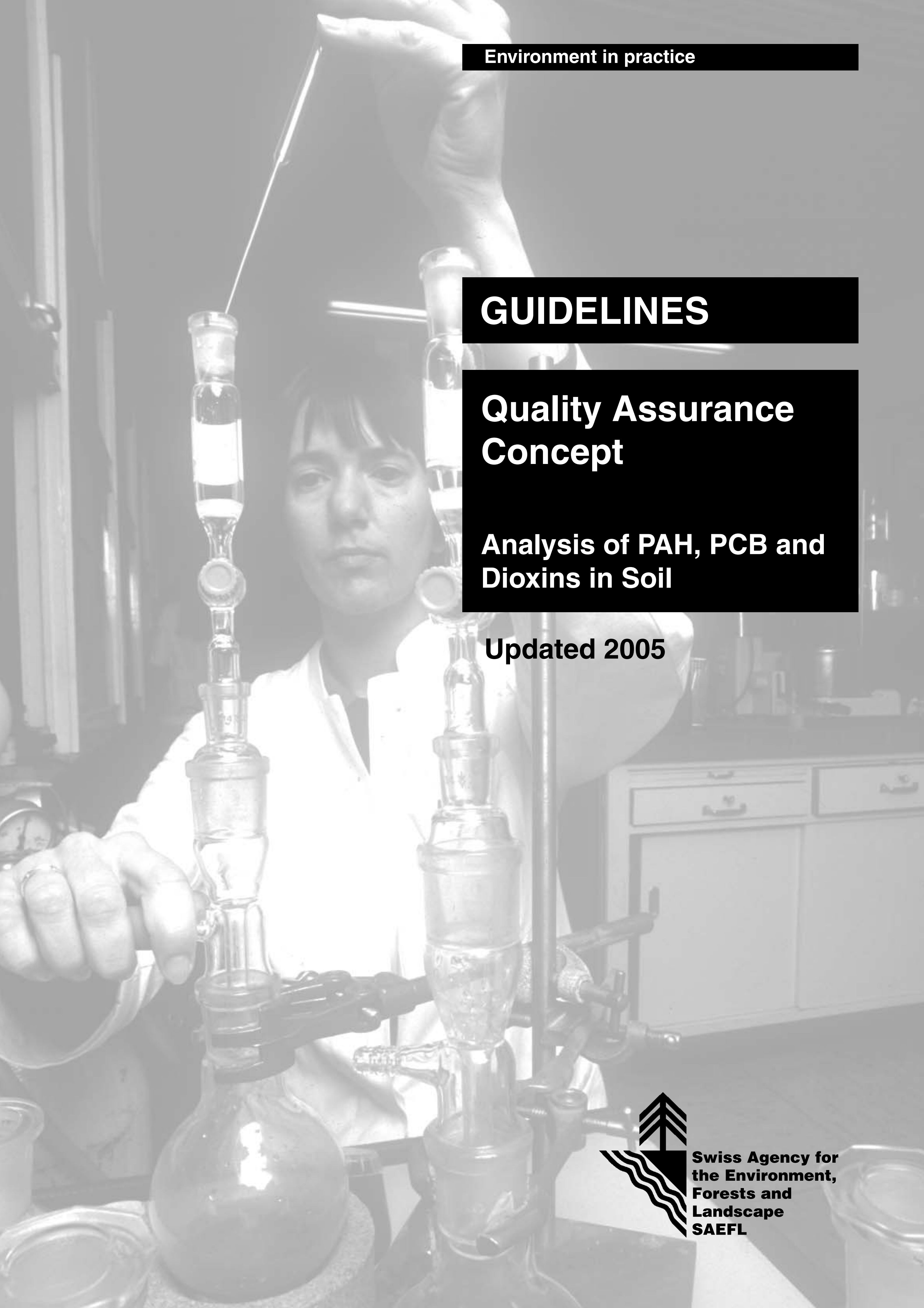

Environment in practice

GUIDELINES

Quality Assurance Concept

Analysis of PAH, PCB and Dioxins in Soil

Updated 2005

Swiss Agency for
the Environment,
Forests and
Landscape
SAEFL

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CONTENTS

ABSTRACTS

A quality assurance concept is presented for the determination of organic pollutants in soil. It is based on a framework of various control criteria, also part of measuring standards, that were published by the *European Committee for Standardization (CEN)* in Brussels. It allows the assessment of the quality of each analytical method for determining PAH, PCB and dioxins in soils. This allows an optimised methodology to be applied to any soil type and measuring techniques to be modified at any time without being tied to a given standardised method. Apart from imperative criteria which must be fulfilled by any method during validation, the present concept contains identification and quantification criteria which must be satisfied for each single compound and sample. Furthermore, terms that must be met by both the blank and the control samples are listed in detail. Both of these are specifically defined for the component and the method. Moreover, an estimation of the measuring uncertainty is included as requested by quality assurance guidelines. In addition, rules are given for keeping records and reporting results. Brief comments are made on analytical aspects of each compound class, and selected literature (up to the year 2004) facilitates the choice of optimal techniques and avoidance of sources of error when developing and optimising methods. A list of methods which fulfil the criteria of the quality assurance concept are available as a separate document.

Keywords: Chemical soil analysis, quality assurance, organic micropollutants PAH, PCB, PCDD/F.

Es wird ein Qualitätssicherungskonzept für den Nachweis von organischen Schadstoffen in Böden vorgelegt, welches auf verschiedenen Kontrollkriterien beruht. Letztere sind auch Teil von Messstandarden, welche vom *Comité Européen de Normalisation (CEN)* in Brüssel erarbeitet worden sind. Das Qualitätssicherungskonzept ermöglicht die Beurteilung der Qualität eines jeden Analysenverfahrens zur Bestimmung von PAK, PCB und Dioxinen in Böden. Damit wird ermöglicht, jederzeit die für einen bestimmten Bodentyp optimale Methodik anzuwenden, bzw. Analysenverfahren entsprechend anzupassen, ohne durch standardisierte Verfahren gebunden zu sein. Neben vorgeschriebenen Elementen, die bei der Methodenvalidierung erfüllt werden müssen, enthält das Konzept Identifizierungs- und Quantifizierungskriterien, welche für jede Verbindung in jeder Einzelprobe erfüllt werden müssen. Weiter werden detaillierte Bedingungen vorgestellt, die bei Blind- und Kontrollproben eingehalten werden müssen. Diese sind sowohl komponenten- als auch methodenspezifisch definiert. Ausserdem wird eine Abschätzung der Messunsicherheit vorgenommen, wie sie von Qualitätssicherungskonzepten verlangt wird. Es werden ebenfalls Vorschriften zur Archivierung und Rapportierung von Resultaten festgelegt. Anhand ausgewählter Literatur (akualisiert bis 2004) sollen generelle, informative Anmerkungen zur Analytik jeder Verbindungsklasse dazu beitragen, einerseits optimale Techniken auszuwählen und andererseits Fehlerquellen bei der Entwicklung und Verbesserung von Analysenverfahren zu vermeiden. Eine Liste von Methoden, welche die Kriterien des Qualitätssicherungskonzepts derzeit erfüllen, ist als separates Dokument erhältlich.

Stichwörter: Chemische Bodenanalyse, Qualitätssicherung, organische Spurenschadstoffe PAK, PCB, PCDD/F.

Ce document présente un système d’assurance de la qualité pour la détection de polluants organiques dans les sols. Celui-ci repose sur un ensemble de critères de contrôle qui correspondent également à une partie des standards de mesures élaborés par le *Comité Européen de Normalisation (CEN)* de Bruxelles. Il permet d’évaluer la qualité de chaque procédé d’analyse destiné à mesurer la teneur des sols en PAH, en PCB et en dioxines. Il est ainsi possible d’utiliser à chaque fois la méthode optimale pour un type de sol spécifique ou d’adapter les procédés d’analyse en conséquence sans être contraint de passer par des procédés standardisés. En plus des éléments nécessaires à la validation de la méthode, le système inclut des critères d’identification et de quantification qui doivent être respectés pour chaque composé dans chaque échantillon. Il présente aussi dans le détail les conditions qui doivent être remplies pour les échantillons témoins et pour les échantillons destinés aux essais à blanc. Ceux-ci sont définis en fonction du composé concerné et de la méthode choisie. Le document présente par ailleurs des prescriptions pour l’archivage et le compte rendu des résultats. Il contient également des remarques d’ordre général et informatif. Celles-ci doivent permettre, grâce à une bibliographie sélective (actualisé 2004), de choisir les techniques optimales et d’éviter des sources d’erreur lors du développement et de l’amélioration des procédés d’analyse. Une liste de méthodes satisfaisant aux critères du système d’assurance de la qualité est disponible sous la forme d’un document séparé.

Mots-clés: Analyses chimiques des sols, assurance de la qualité, micropolluants organiques PAH, PCB, PCDD/F.

Questo documento presenta un concetto di Quality Assurance (assicurazione della qualità) per la determinazione dei prodotti organici nocivi presenti nel suolo. Tale concetto è basato su un insieme strutturato di criteri di controllo che fanno pure parte di standard di misura elaborati dal *Comité Européen de Normalisation (CEN)* di Bruxelles. Esso permette di valutare la qualità di ogni metodo analitico per la determinazione di PAK, PCB e diossine presenti nel suolo. È quindi possibile utilizzare la metodologia più adatta per un determinato tipo di suolo ed adattare in ogni momento i procedimenti analitici, senza essere vincolati da un metodo standardizzato. Oltre alle condizioni prescritte che ogni metodo deve rispettare durante la fase di convalida, il concetto comprende anche i criteri per l'identificazione e la quantificazione: ogni composto di ogni singolo prelievo deve soddisfare questi criteri. Il concetto elenca inoltre le condizioni precise che le prove in bianco ed i campioni di controllo devono soddisfare. Tali condizioni sono definite in modo specifico sia per i composti che per i metodi. Sono state pure formulate delle prescrizioni relative all'archiviazione dei dati e alla comunicazione dei risultati. Le informazioni d'ordine generale concernenti l'analitica di ogni classe di composti, corroborate da indicazioni bibliografiche aggiornate sino al 2004, dovrebbero permettere di selezionare le tecniche analitiche più idonee e di evitare fonti di errori durante lo sviluppo e l'ottimizzazione dei metodi analitici Un elenco dei metodi che soddisfano i criteri del concetto di Quality Assurance è ottenibile sotto forma di documento separato.

Parole chiave: analisi chimica del suolo, assicurazione della qualità, microinquinanti organici PAH, PCB e PCDD/F.

FOREWORD

In collaboration with the *Institute of Organic Analytical Chemistry* of the University of Basel, a scheme for assuring the quality of soil analyses has been developed. The present publication is an initial step towards establishing a compendium of methods on the preparation and analysis of organic pollutants as required by the *Ordinance of 1 July 1998 relating to impacts on the soil (OIS'98)*. Publications of methods for the determination of PAH, PCB and PCDD/F were carried out in 2001–2003. The present amended *Quality Assurance Concept* replaces the SAEFL guidelines *Quality Assurance Concept* of January 2000.

There never were plans to establish a mandatory «federal method» for the various substances relevant to the soil. However, Prof. M. Oehme from the Institute mentioned above presents here minimum requirements that may allow organic micropollutants in the soil to be extracted and analysed as completely as possible (total content). Those methods should wherever possible be used in any laboratory equipped with state-of-the-art technology.

It is our particular concern to avoid hindering the technical development of trace analysis. Nevertheless, we wish to ensure that all analytical results are comparable and reproducible.

In view of the politically sensitive nature and the financial consequences of control measures that may be involved if guide, trigger, and clean-up values are exceeded (see OIS'98), the question of quality assurance is essential and mandatory, and has to be updated regularly as has now been done with the first issue of the said guidelines of January 2000.

I should like to very warmly thank all those who have contributed towards this revised report in one way or another.

Georg Karlaganis

Head of the Department for Substances,
Soil, Biotechnology

Definitions

Clean-up standard	Isotope-labelled or other internal standards added prior to sample clean-up. They allow to correct for losses during this and the following procedures.
Congeners	Compounds with identical carbon skeleton but different number of e.g. chlorine substituents.
Extraction blank	Value determined by a blank sample covering the complete analytical procedure including extraction, cleanup, identification and quantification as well as all the relevant reagents and materials.
Extraction standard	Isotope-labelled or other internal standards added prior to extraction and used for calculation of results. They allow to compensate for losses during extraction and clean-up.
Field blank	Value determined by a blank sample covering a special procedure used to ensure that no significant contamination has occurred during all steps of the measurement and to check that the operator can achieve a quantification level adapted to the task.
Isomers	Compounds with identical carbon skeleton and same number of e.g. chlorine substituents at different positions.
Keeper	High boiling solvent to be added to the sample extract to prevent evaporation losses.
Recovery standard	Isotope-labelled or other internal standards added to the sample extract prior to injection into the GC. They allow to calculate losses of extraction and clean-up standards.
Spiking	Addition of isotope-labelled or other internal standards to a sample or sample extract.

Symbols and abbreviations

ASE	Accelerated solvent extraction
CEN	Comité Européen de Normalisation (European Committee for Standardization) in Brussels
DIN	Deutsches Institut für Normung (German Institute for Normalisation)
ECD	Electron capture detector
EI	Electron ionisation
EN	European Norm
FBE	Fluidised bed extraction
GC	Gas chromatography
GC-ECD	Gas chromatography – electron capture detection
GC-MS	Gas chromatography – mass spectrometry
GPC	Gel permeation chromatography
HpCDD	Heptachlorodibenzo-*p*-dioxin
HpCDF	Heptachlordibenzofuran

HPLC	High performance liquid chromatography
HRGC	High resolution gas chromatography
HRMS	High resolution mass spectrometry
HxCDD	Hexachlorodibenzo-*p*-dioxin
HxCDF	Hexachlorodibenzofuran
ISO	International Standardisation Organisation
ISTD	Internal standard
I-TE	See I-TEF
I-TEF	International toxic equivalent factor according to the international model relative to 2,3,7,8-TCDD
I-TEQ	International toxic equivalent obtained by weighting the mass determined with the corresponding I-TEF according to the international model relative to 2,3,7,8-TCDD
LRMS	Low resolution mass spectrometry
MS	Mass spectrometry
NICI	Negative ion chemical ionisation
OCDD	Octachlorodibenzo-*p*-dioxin
OCDF	Octachlorodibenzofuran
OIS	Ordinance Relating to Impacts on the Soil
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PCDD/PCDF	Polychlorinated dibenzo-*p*-dioxins and dibenzofurans
PeCDD	Pentachlorodibenzo-*p*-dioxin
PeCDF	Pentachlorodibenzofuran
PFK	Perfluorokerosene
ppt	«*parts per trillion*», concentration unit, corresponds to 1 picogram (10^{-12} g) per g
PFTBA	Perfluorotributylamine
ppb	«*parts-per-billion*», concentration unit, corresponds to 1 nanogram (10^{-9} g) per g or 1 µg/kg
SFE	Supercritical fluid extraction
SIM	Selected ion monitoring
u	Abbreviation for atomic mass unit on the basis of the Carbon atom, $^{12}C = 12.00000$ u
TCDD	Tetrachlorodibenzo-*p*-dioxin
TCDF	Tetrachlorodibenzofuran

1 Introduction

11 Preliminary comments

Soil is a very heterogeneous matrix, which often presents problems in the analysis of environmentally hazardous organic pollutants at trace levels. Variation in the proportional composition of organic and inorganic main constituents could be the basis for systematic errors. The reason may be found in the different matrix residues or loss of compounds even when using standardised and validated methods. A higher ratio of clay/silt may also cause a higher adsorption of the chemical compounds being analysed because of the increased number of ion exchange centres present. The subsequent extraction of such compounds from the sample matrix is made more difficult.

The variable content of organic carbon in soils and its chemical composition, as well as inorganic carbon (carbonate) content, will also affect the efficiency of extraction and clean-up. Incomplete separation of the analytes from organic compounds of highly similar polarity and structure could cause a higher background. Furthermore, graphite-like structures are present to which planar aromatic structures such as polycyclic aromatic hydrocarbons or polychlorinated dibenzo-*p*-dioxins may strongly adsorb.

As a consequence, the analytical methods applied here must be adjusted to the qualities of the sample matrix, and must also be modified and optimised continuously. Providing a standard working procedure defined in every detail is thus not very useful.

A basic quality assurance concept must be made available to cover the various analytical methods used and their continuous modification. This quality assurance concept may allow the quality evaluation and assessment of a specific method to be judged. The concept also includes guidelines and criteria for the validation of a method and provides minimum quality standards that must be met.

For these reasons, some analytical standards including a general quality assurance concept are being drafted by the *European Committee for Standardization (CEN)* in Brussels. Its requirements must be met by any method used. Laboratories must provide proof by means of an internal validation, completed by participating in interlaboratory validation and intercalibration exercises.

Furthermore, quality control criteria are given, which must be met by every single sample. Examples for methods which satisfy such quality requirements are listed. These methods may - but not necessarily must – be used. Any method that has been proven to meet the defined criteria is also authorised.

This concept has been accepted for the methodological paragraphs of the *Ordinance of July 1998 relating to impacts on the soil (OIS'98).* Where possible, the criteria of existing concepts and standards were included. The initial chapters of this quality control and assurance concept are valid for all organic micropollutant classes in question (PAH, PCB, PCDD/PCDF). Specific requirements or deviations from the present quality assurance concept of these micropollutants are listed, if necessary, in subsequent subchapters.

The revision of the CEN standard EN-1948 parts 1–3 in 2004 made it necessary to adapt some of the QC standards in the *«Quality Assurance Concept – Analysis of PAH, PCB and Dioxins in Soil»* issued in January 2000. Moreover, some definitions of terms were changed. According to the ISO 17025 standard for accreditation of measuring laboratories the determination of the measuring uncertainty of analytical methods is now mandatory. Therefore, this issue presents an update of the points mentioned above. Moreover useful information in the informative part as well as references were updated up to 2004.

12 Principal comments on the quality assurance concept

The quality assurance concept is valid only for the following persistent organic compounds:

- Polycyclic aromatic hydrocarbons (PAH),
- Polychlorinated biphenyls (PCB), and
- Dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF).

The quality assurance concept comprises all steps of the sample pre-treatment, extraction, clean-up, separation, identification and quantification. The specifications of guidelines being drafted and of the OIS'98 for soil sampling must be met.

The following points are summarised:

- In accordance with CEN only the quality assurance concept is mandatory. Comments are for information only.
- A separate list of working procedures is published in parallel which meet the requirements of the quality assurance concept. This list is updated periodically, and will also be for information only. This list of methods may be supplemented at any time by new methods, as long as they meet the minimum provisions of the present quality assurance concept.
- The quality assurance concept lists minimum requirements which must be satisfied by all methods used. Such procedures are usually evolving with respect to specific experiences and set accordingly. However, the provision of more stringent method standards exceeding those defined here is permitted.

2 Elements of the method and quality assurance concept

21 Preliminary comments

The basis of the «Quality Assurance» concept discussed here is the use of internal reference standards which are added to the sample at different steps of its handling. This methodology is mandatory. They allow losses of compounds at different steps of the sample pre-treatment to be identified and quantified. Furthermore, interference by residues of the sample matrix can be detected with the help of such standards. Finally, these added reference compounds serve as internal standards for quantification. In this way, minor and still acceptable compound losses are corrected automatically. The losses of internal reference standards during the clean-up procedure are determined by adding an internal recovery standard. *Table 1* gives a summary of the use of these internal reference standards.

Each quality assurance concept defines standards that any chosen method must meet before it can be used in real samples (**method validation**). Furthermore, each sample analysed must be subject to an assessment of the reliability of the results obtained (**quality control**). Criteria for identification, quantification and acceptance are defined, and must be met.

Table 1: Designation of an internal standard with emphasis on its application.

Point at which standards are added	Term	Purpose
Prior to the sample extraction (dried sample)	extraction standard	allows losses occurring in extraction and clean-up to be corrected
Prior to the sample clean-up	clean-up standard	allows losses occurring in clean-up to be corrected
Prior to the quantification	recovery standard	allows losses occurring in preceding steps to be calculated

22 Method validation

221 Preliminary comments

Before using a method for analysing samples, the performance of the method must be evaluated carefully. Validation through systematic studies in the laboratory must be carried out to confirm that the method meets the requirements.

The **method validation** shall include the following points:

- Determination of selectivity;
- Linearity range;
- Limits for detection and quantification;
- Robustness of the method to small changes of method parameters or of sample composition;
- Precision and reproducibility.

Procedures normally applied during a method validation are:

- Determination of recovery of known quantities added to a sample;
- Comparison of results with those of an independent (validated) method;
- Analysis of certified reference materials, and
- Multiple standard addition to real samples.

Moreover, it must be shown that the method meets all the criteria mentioned in the chapters below.

222 Drying of samples

The provisions of the guidelines on soil sampling must be met (cf. *«Manual – Sampling and sample pre-treatment for soil pollutant monitoring»; SAEFL 2003).*

223 Sample extraction

The efficiency of any sample extraction procedure (soxhlet extraction, liquid/liquid extraction, accelerated solvent extraction etc.) must be documented as follows:

- Using the same method, the second extract of a sample extraction shall not contain more than 5 % of the quantity of a specific compound from the first extraction. This standard must be met by any compound to be quantified.
- If there are doubts as to the extraction efficiency of a method, proof must be given that another method shown experimentally to be comparable allows the requirements of the previous paragraph to be fulfilled. The same applies to any other solvent with a higher solvent strength and/or increased π-electron interactions.

  Example: If methylene chloride is used as a solvent for soxhlet extraction it must be shown that this procedure yields extractions comparable to the application of toluene as a solvent for soxhlet extraction. The requirements mentioned in the first paragraph are not met if the extraction period is too short or if the number of extraction cycles are too low (liquid/liquid extraction).

The efficiency of the sample extraction must be documented as an integral part of the method description. It must be checked at regular intervals, and must also be restored after each modification.

Furthermore, the efficiency of the sample extraction must be monitored for each sample individually by adding suitable compounds prior to the extraction as an internal extraction standard.

224 Sample clean-up

The clean-up method used depends on the type of sample matrix that has to be removed. The composition and quantity of interfering compounds may vary considerably among samples. It is not normally possible to use a precisely defined clean-up method for all samples. Minor modifications are often necessary. The following basic quality control criteria were set; they must be documented for each clean-up method:

- The recovery rate of all compounds to be quantified must be determined.
- The recovery rate for method validation must be between 70 % and 115 %.

These method criteria must be checked and documented anew after each modification of the clean-up procedure. The clean-up of each sample must be checked individually. For this purpose, suitable compounds are added as clean-up standards prior to the sample clean-up.

3 Identification criteria for compounds

31 Preliminary comments

Those detection methods are to be preferred that produce information which allow to identify a compound in the most unequivocal way. The use of detectors measuring not very characteristic compound properties or having a rather limited linear range should be restricted. When using non-specific and/or low selective or linear detectors (flame ionisation detector, electron capture detector, fluorescence detector), the linearity shall be controlled regularly by multiple standard addition. Furthermore, it has to be ensured that no interferences are present by control of the separation on two different stationary phases and by comparison with other independent methods.

32 Mass spectrometry

For the mass spectrometric detection of chlorinated compounds at least two ions of the chlorine isotope pattern of the molecular ion or the most abundant fragment ion shall be recorded for each congener. This is valid both for ^{12}C-congeners as well as for ^{13}C-isotope labelled congeners. For PAH the M^+- and $(M\text{-}C_2H_2)^+$-ion may be selected.

A compound is only considered as unambiguously identified, if all of the following criteria are fulfilled:

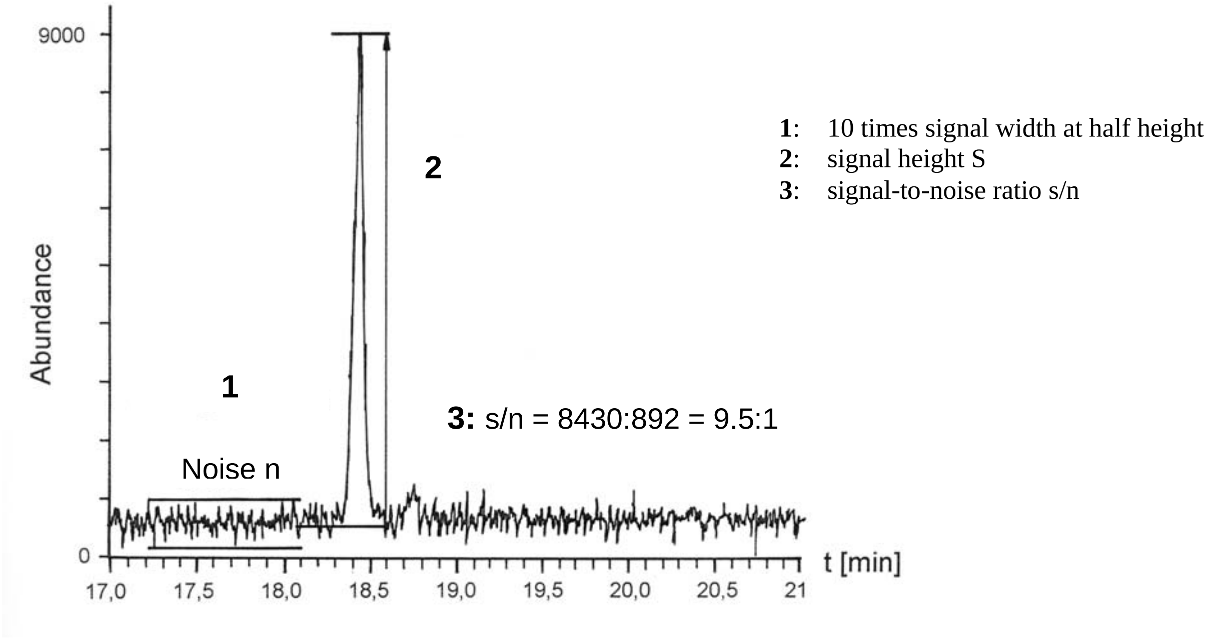
- The abundance ratio between isotope or fragment ions shall match the theoretical value within 20 %.
- The base line noise shall be measured in front of the signal of the analyte within a signal-free window corresponding to 10 times the signal width at half height. Peak-to-peak values are taken. The signal-to-noise ratio of the raw data as documented in *Figure 1*, shall be at least 3:1 for the signal used for quantification. A noise smoothing over 3 measuring points is allowed.

33 Electron capture and flame ionisation detector

The following requirements must be fulfilled when determining PCB with electron capture detection or PAH with flame ionisation detection:

- Since a compound is identified by retention time only, the analysis has to be carried out on two stationary phases of different polarity.
- The deviations of the relative retention times based on the internal standard and compared with the analysis of a calibration standard must not be more than ±0.3 %.

Figure 1: Definition and determination of the signal-to-noise ratio. The signal-to-noise ratio S/N shown in the figure is 10:1.



1: 10 times signal width at half height
2: signal height S
3: signal-to-noise ratio s/n

34 Fluorescence detection

The determination of PAH with fluorescence detection must meet the following criteria:

- The retention time of a PAH with respect to the retention time of the quantification standard must be within a relative retention time window of ±1.5 %.
- Signal quenching or co-elutions might cause systematic errors. Therefore, in case of doubt, the complete fluorescence emission spectrum must be recorded.

4 Quantification criteria

Since interferences due to matrix effects can never be excluded, quantification shall only be carried out by the **internal standard method**. In addition to the requirements for identification described in paragraph 3, the following points shall be fulfilled as quantification requirements:

1. The compound to be analysed shall be separated from all other interfering signals within a 25 % valley below the top of the minor peak with respect to the height of that peak. An exception are some benzofluoranthenes, which cannot be separated from each other. In this case a too high («false positive») result has to be expected due to the additional areas of other not separated benzofluoranthenes. This is normally insignificant.

2. The recovery rates of the internal standards added prior to clean-up shall be within 50–115 %.
3. The signal-to-noise ratios of the internal standards used for quantification shall be >20:1.
4. The concentration differences between the internal standards added to the sample and the calculated concentrations shall not exceed a factor of 20.
5. The measuring range shall be linear (at least over a concentration range of a factor of a 100). The standard deviation of the relative response factor shall not exceed 15 % and shall be based on a minimum of five measuring points over the whole range.
6. An extraction blank shall be taken. The blank of all compounds to be analysed shall be equal or less than the detection limit of the method. Alternatively, the levels found shall be at least a factor of 10 below the lowest measured concentrations in the series of samples.
7. **Mass spectrometry only:** The peak shape of the gas chromatographic signal of a compound shall contain ten or more sampling points. Otherwise the peak shape cannot be reconstructed precisely enough, and the correct peak areas or heights cannot be calculated sufficiently exact.
8. **Fluorescence detection only:** The linearity within the calibrated measuring range shall be controlled with real samples and multiple standard addition of known concentrations.
9. Quantification is based on two isotope ions. *Note:* If quantification is possible only with one single ion in case of interferences on the second trace, this has to be reported.

5 Quality assurance criteria

51 Reference compounds for quantification

- Only reference compounds or solvents with a precisely known, and if possible certified, purity (minimum ≥95 %, if available ≥99 %), or concentration shall be used.
- Primary reference standards should be stored at a maximum temperature of 4 °C. To avoid solvent losses by evaporation, only specially made vials with capillary opening such as the CERTAN®-vial*), or ampoules sealed by melting, should be used.
- The weight of the container including the reference solvent shall be determined prior to use, and if necessary be corrected by adding solvent.
- The concentrations of newly prepared dilutions shall be compared to those currently in use. Differences and systematic deviations over time shall not exceed the measuring precision of the method.

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*) CERTAN® is the trade name of a product supplied by LGC-Promochem, Germany. This information is given for the convenience of users of the quality assurance concept and does not constitute an endorsement by SAEFL of the product named. Equivalent products may be used, if they can be shown to produce the same results.

52 Control of the method blank

Blanks of all compounds to be quantified shall be checked for the complete analysis method (extraction, clean-up, separation, quantification), in the following cases:

- After a series of no more than 10 samples.
- After major changes in the extraction or clean-up procedure such as:
  - use of new or modified equipment;
  - use of new batches of solvents or adsorbents.
- After the analysis of a sample with unusually high concentrations exceeding average concentration levels of previously analysed samples by a factor of 10.

Field blanks should be taken during each sampling. A field blank follows the exact procedure at real sampling (same equipment, same type of sample bottle).

Sand scorched in the laboratory is used as a synthetic matrix (see *Chap. 53).*

The results of a blank may only be accepted if all criteria given here are met:

- The blank of all compounds to be quantified shall either correspond to the detection limit at a signal-to-noise ratio of 3:1, or the values found shall be lower by at least a factor of 10 than the lowest value to be expected in real samples.
- The recovery rate of the internal standards added prior to the clean-up shall be within 50 and 115 %.

53 Control of the blank of the entire method

The blank of the entire method (field blank) includes also the control of possible contamination during sampling or by the sampling equipment. Solvents used for a final rinsing have to be stored for a possibly later control of the sampler blank. The blank of this rinsing has only to be determined, if results exceed e.g. a trigger value.

The field blank procedure consists in the whole measuring procedure including sampling (see *Chap. 52).* A field blank procedure shall be performed at least before each measurement series.

Before new samples are taken with the same sampling equipment, it has to be cleaned thoroughly. A final rinse of all surfaces reused, which are in contact with the sample, shall be performed. The rinsing solution shall be stored. It shall be analysed, when the concentration of the following sample exceeds a trigger value or if there are doubts about their correctness. If the sampler blank contains levels, which are higher than a trigger value, the sampling has to be repeated.

If several measurements are performed at the same time and according to the same procedure, and if the measurements are performed on the same site, then a single field blank is sufficient.

The field blank shall not be deducted from the measured value.

54 Analysis of control samples

A certified reference material or an aliquot of a large quantity of a homogeneous raw extract must be analysed at least 5–10 times annually. The results must meet the following criteria:

- The standard deviation of the annual control series shall not exceed the reproducibility (repeatability) or accuracy observed in earlier series. The highest value has to be taken.
- The absolute deviation of the average annual values shall be similar to the accuracy of the method. No systematic trend must occur.

55 Further recommendations

- **Control of results using an independent method:** Comparing the applied quantification method to a selected number of samples with a second and independent technique (e.g. a second stationary phase and/or detection method) is recommended.
- **Intercalibrations:** The comparability of analytical results shall be monitored between laboratories. Raw extracts (without additional concentration increase) shall be mailed together with the corresponding quantification standards. The laboratories must also report the deviations between the standards offered and their own standards. Deviations of up to ±10 % for standards and up to ±20 % for extracts are considered acceptable.

6 Measuring uncertainty

61 Preliminary comments

ISO17025 as well as CEN requires that the measuring uncertainty of a method is estimated and/or (semi)quantitatively determined. The main problem is to detect the influence of systematic errors. The procedure given below should help to determine the measuring uncertainty of any method following this guideline.

It also lists typical errors of procedures as an aid as well as an example for the determination of the measuring uncertainty, which was adopted from EN-1948-3 Annex A and correspondingly modified. *Chapters 62* and *63* give a general survey about different types of errors and their range. In *Chapter 64* the measuring uncertainty for the determination of polychlorinated dibenzo-*p*-dioxins and dibenzofurans is estimated as an example. Similar estimates can be carried out for the analysis of PCB and PAH as briefly outlined in *Chapter 65*. In general, the measuring uncertainty of any in-house method should be determined and compared with the achieved precision/accuracy (e.g. from control samples or intercalibrations).

62 General aspects

Prior to carrying out the estimation of the overall measuring error (measuring uncertainty) of a measuring technique, all error sources which might contribute to the overall uncertainty have to be listed, classified and their size determined or estimated.

There are two types of errors influencing the measuring result:

- Random errors (type A);
- Systematic errors (type B).

Only the dimension of random errors can be determined experimentally by carrying out several parallels and calculating e.g. the standard deviation. Type B errors can only be estimated since the true value of a concentration usually is not known. *Table 1* lists some important errors contributing to the measuring uncertainty and its type.

Table 1: Classification of type of error introduced by some important parameters of a method contributing to the overall measuring uncertainty.

Part of method	Contributing parameter	Type of error
Sampling	Not representative sampling Sample inhomogenities Contamination (sampler)	A/B A/B B
Sample pretreatment	Extraction Column chromatography (e.g. activity adsorbence) Loss during sample concentration	A/B B B
Preparation of reference solutions	Certified value of standard Dilution	A/B A
Quantification	Matrix effects Signal integration Interferences	B A/B B

The mathematically correct approach to estimate the overall measuring error of a method is to establish a formula including all parameters necessary for the result calculation. It is then differentiated for each variable. This is often practically impossible. Therefore, assuming parameters independent from each other, the overall measuring uncertainty can also be estimated by adding the squares of all errors and calculating the square root of the sum. Partial errors can be summed up in this way as well.

63 Dimension of errors

631 Type A errors

For a first dilution of primary reference standards, a volume is transferred to a volumetric flask. The weight of both the containers of the reference standards and of the volumetric flask are determined after each volume addition. The precision of this operation is 1–2 % as checked experimentally. The precision of the volumetric flask is 1.5 % (in laboratory tests). A second dilution is necessary to obtain quantification, internal or recovery standards.

The weighing error of solid material is within 0.2–2 % depending on the precision of the balance.

A volume around 10 µL of an internal standard solution is added. The precision obtained with a syringe is 1.0 %. The same is valid for the volume of the recovery standard (10 µL) which is added prior to the GC/MS-analysis.

The signal area determination of the gas chromatographic signal has a precision of 2–5 % depending on the signal shape.

632 Type A+B errors

The following operations have a random error which is either not directly accessible experimentally, since the above listed errors contribute during their determination or they include a systematic error which cannot be determined either. Therefore, the errors given below are estimates based on data achieved during method validation, where only parts of all method steps were included (e.g. recovery study of sample clean-up without extraction and with only analyte spikes):

- The precision of a GC/MS-analysis is in the range of 5–10 %.
- Typical precision of sample clean-up including GC/MS-analysis is in the order of 15 %. It is estimated to be around 15 % net including a systematic error.
- The repeatability of the overall analytical method (sampling not included) in trace analysis (very low ppb range) is around 10–15 %, when the same sample is analysed five times.

633 Type B errors

Systematic errors of a given maximum value are introduced due to measurable blanks (up to 10 % are acceptable) and deviations in the concentrations of reference standards. The latter is usually not well known, unless the supplier guaranties a maximum divergence. Usually, according to supplier certificates, the accuracy/precision of commercial reference standards in solution is in the range of 5–10 %.

64 Estimation overall measuring uncertainty: PCDD/PCDF in soil

641 Without reference standard accuracy

This example describes the estimation of the overall measuring uncertainty in detail. As a first step the uncertainty is estimated concerning the preparation of the calibration standard (error E_{STD}), internal standard (E_{ISTD}) and recovery standard (E_{REC}). For each standard two dilution are necessary introducing the error E_{v1s}, E_{v2s} (error volume transfer 1 and 2; 2 % each) as well as E_{v1m}, E_{v2m} (error measuring flask 1 and 2; 1.5 % each). The total uncertainty for E_{STD}, E_{ISTD} or E_{REC} is:

$$E_{STD} = \left[(E_{v1s})^2 + (E_{v1m})^2 + (E_{v2s})^2 + (E_{v2m})^2\right]^{1/2} \qquad \text{(B.1)}$$

$E_{STD,\ ISTD,\ REC}$ = 3.53 %

The uncertainty $E_{f(i)}$ concerning the calculation of the response factor f_i includes the error of the concentration of the ^{12}C-isomer (i) ($E_{STD}{}^{12}C_i$) and the ^{13}C-isomer (i) ($E_{STD}{}^{13}C_i$) as well as the error of the corresponding signal areas $E_A{}^{12}C_i$ and $E_A{}^{13}C_i$. E_A is about 2 % and E_{STD} 3.5 %. This gives for $E_{f(i)}$:

$$E_{f(i)} = \left[(E_{STD}{}^{12}C_i)^2 + (E_{STD}{}^{13}C_i)^2 + (E_A{}^{12}C_i)^2 + (E_A{}^{13}C_i)^2\right]^{1/2} \qquad \text{(B.2)}$$

$E_{f(i)}$ = 5.74 %

$E_{M(i)}$ is the uncertainty of the calculation of the total quantity of M_i of an isomer (i) in the sample. It is composed of the errors $E_{f(i)}$ of the calculation of the response factors f_i, the volume error $E_V{}^{13}C_i$ of the ^{13}C-isomers (i) used as internal standard and the errors of the signal areas $E_A{}^{12}C_i$ and $E_A{}^{13}C_i$. E_A was determined as about 2 %, $E_{f(i)}$ as 5.7 % and E_V as 1 %. $E_{M(i)}$ is then:

$$E_{M(i)} = \left[(E_V{}^{13}C_i)^2 + (E_{f(i)})^2 + (E_A{}^{12}C_i)^2 + (E_A{}^{13}C_i)^2\right]^{1/2} \qquad \text{(B.3)}$$

$E_{M(i)}$ = 6.48 %

For the calculation of the concentration c_i of isomer (i) in a sample the error E_{Ve} in the amount has to be included which was determined as about 2 % including rest humidity and weighing error. The overall measuring uncertainty $E_{c(i)}$is then:

$$E_{c(i)} = \left[(E_{Ve})^2 + (E_{M(i)})^2\right]^{1/2} \qquad \text{(B.4)}$$

$E_{c(i)}$ = 6.78 %

In addition, an overall contribution from type B errors is estimated to be in the order of 10 %. This gives a total measuring uncertainty E_{sum} of:

$$E_{sum} = \left[(E_{c(i)})^2 + (E_{Met})^2\right]^{1/2} \qquad \text{(B.5)}$$

E_{sum} = 12.08 %

642 Implementation of uncertainty of reference standards

The uncertainty of the concentrations of purchased reference standards has also to be included though it is not part of the measuring technique and cannot be influenced either. A further systematic error of 5 % has therefore to be added to the measuring uncertainty evaluation resulting in a possible measuring error E_{tot} of 15–20 %.

E_{tot} = 15–20 %

643 Conclusion

The estimated measuring uncertainty of 12 % agrees well with results from method intercalibrations (no sampling included) where results were determined based on a calibration standard in common for all participants. The observed range of the coefficient of variation was 10–40 %. Most results were within 20 % or less.

Based on the overall estimation and the results of intercalibration the measuring uncertainty of the analytical method including sample amount determination is in the order of 15 % within the same laboratory. The interlaboratory measuring uncertainty is in the range of 15–25 %.

65 Corresponding estimations for PAH and PCB in soil

An estimation of the measuring error of concentrations of PAH and PCB can be carried out correspondingly. Since the analytical methodology is quite similar to that for PCDD/PCDF, the same approach can be used. Measuring errors of dilutions are the same, so that the estimated error of this part has only to be adapted to the overall numbers of dilutions. Also the errors introduced by signal area integration and weighing can be taken. The only part which is different, is the contribution of type B errors under B.5. Here, an overall addition of around 5–10 % can be estimated due to higher concentrations than for PCDD/PCDF and a correspondingly lower risk due to interferences by the sample matrix. The uncertainty of the concentrations of purchased reference standards is comparable to that of PCDD/PCDF. Therefore, also here a further systematic error of 5 % can be added to the measuring uncertainty evaluation.

The error E_{sum} is therefore somewhat lower and in the range of 5–10 % as well as E_{tot} within 10–15 %.

7 Record keeping and reporting

71 Filing of data

For formal reasons the time periods required by the accreditation authorities or by other certification bodies override the limits given in the present document.

If no such statements are forwarded the following time periods are effective:

- Written information about chromatographic separations, detector optimisation and operational parameters must be kept for at least **one year**.
- Raw data which allow such information to be reconstructed must be kept on a secure electronic back-up medium for at least **five years**.
- The print-out of all data needed for the calculation of the concentration of a sample must be kept for at least **two years**.
- The data must also be kept available on a secure electronic back-up for at least **five years**.

The same time periods are effective for calculations and controls of calibration standards, blanks and recovery rates.

72 Reporting

A report of results must contain the following information:

- The measuring data shall be given as a quantity per sample quantity, without any blank deductions, and corrected with respect to the recovery.
- Recovery rates of internal standards added prior to the extraction and clean-up shall be listed.
- Data that do not meet all the quality control criteria shall be flagged.
- Limits of detection must be specified.
- All exceptions and deviations from the standard procedure must be listed.
- A short but precise description of the entire method shall be included (a detailed report shall be available on request).

If required, the following information must be available:

- The origin of and control procedure for quantification and reference standards and of certified reference material.
- Measured blank data of the respective sample series, including values of method and field blanks.
- Information about results of control samples analysed in the course of the measuring series, and/or information about participation in intercalibration experiments during the preceding year.

8 General recommendations and comments for information only

81 Preliminary comments

As an introduction, some aspects that are important for the analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF), polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) are discussed.

82 Control standards

As specified below in detail for the different compound groups, there are only a few certified reference soil materials available that are suitable for use as method controls. Moreover, some material has such a high contamination level that it is not suitable for normal control purposes. Therefore, it is recommended that a few kilograms of a soil sample are prepared for use as a control. After drying and sieving, this control sample is homogenised with about 10 % of water-free sodium sulphate in order to keep it dry during storage in sealed, airtight containers. The concentrations need not be absolutely correct (e.g. some losses during drying may be accepted), but they must be stable over a long period of time (months, years). This sample may be analysed (e.g. after every 10th–20th real sample). As a possible alternative, a raw extract may be prepared that is frequently cleaned-up and analysed.

83 Removal of sulphur

Relatively high quantities of elemental sulphur (mainly as S_6–S_8) and organic sulphur compounds may be found in soil. Such compounds are difficult to remove with normal liquid chromatography. They may interfere severely in the gas chromatographic separation. Most clean-up methods therefore include a sulphur removal step. Copper powder is often used (during soxhlet extraction, see *Ayris et al. 1997;* or in column chromatography, see *Pavoni et al. 1991).*

However, the copper organic compounds produced in such a process may subsequently interfere at the clean-up steps. Moreover, a risk of self-ignition may arise with the use of pyrogenic copper *(European Standard EN ISO 6468, 1996)*. *Goerlitz* and *Law (1971)* recommend the use of elemental mercury. Although this method may be very efficient it is questionable from a toxicological point of view.

Generally, the most proven methods precipitate sulphur as sulphide or bind it chemically (see e.g. *Jensen et al. 1977).*

84 Determination of polycyclic aromatic hydrocarbons (PAH)

841 Preliminary comments

A comprehensive literature has been published on the determination of PAH. However, many of the published methods have never really been validated, do not satisfy common quality control demands, are complex and time-consuming, or are simply outdated. Quantification (e.g. with high performance liquid chromatography or fluorescence detection) is based on external standard quantification – as are most HPLC techniques. Control of the extraction efficiency and determination of losses during clean-up are thus not possible. On the other hand, the internal standard method could easily be used (see below).

Specific problems of PAH analysis are discussed below. Only literature that covers important notes about methods is cited.

842 Sample extraction

There is a varied literature comparing different extraction methods for PAH in soil, but quite differing results are reported. In principle, a control using spiked soil sample material does not reflect reality. Added PAH in many cases only adsorb superficially onto the soil matrix. They can therefore be extracted more easily. Moreover, varying results may be obtained depending on the soil type applied.

The *Institute for Environmental Protection and Agriculture (IUL/Agroscope FAL Reckenholz)* in Zurich-Reckenholz has published a summary report of a method comparison for PAH in soil (see *Agroscope* FAL papers; *Hort et al. 1998).* The assessment made is basically sound. However, some supplementary comments are necessary:

- Drying of the soil must be carried out at the lowest possible temperature to avoid evaporation of highly volatile PAH (naphthalene) and losses due to increased adsorption of less volatile PAH (more active surface due to removal of molecularly bound water). For ordinary soils not specially rich in humus 40 °C is quite sufficient.
- Annex 2 chapter 2 of the OIS'98 specifies that the extraction must be as complete as possible (organic micropollutants). This provision is met in principle by soxhlet extraction, SFE and ASE *(Heemken et al. 1997).* The extraction yield may be enhanced by preliminary methanolic saponification. However, biogenic PAH may also be released and extracted. In contaminated soil its contribution is neglectable compared to that of the anthropogenic PAH.
- *Szolar et al. (2002)* could show that a modern high speed soxhlet extractor allowed to extract PAH within 90 min when ethylacetate was used. No influence of water was observed, so that normally dried soil could be used without further treatment with sodium sulphate.
- The study of *Song et al. (2002)* demonstrated that ultrasonic extraction was most efficient in recovery compared to soxhlet and simple shaking. However, *Leonhard* and *Stahl (1998)* showed that ultrasonic extraction with chlorinated solvents destroys PAH. Therefore, such solvents should be avoided. Contradictory results might indicate a competitive influence on such degradations by a variable activity of the soil surface.
- In the OSBO study *(OSBO 1997),* various extraction methods are compared in terms of efficiency and robustness. This important source of information should be consulted prior to selecting an extraction method. The OSBO recommendations are briefly summarised as follows: the matrix effect may be substantial, if SFE is used. Once optimised, a method should be checked again prior to extraction of a soil sample showing a clearly different matrix. Soxhlet extraction is still the most robust extraction method for soil, although it does not always yield the best extraction results.
- Contradictory results have been published on SFE. Different adsorption capability and variable water residues of the soils examined are the most probable causes. *Schleussinger et al. (1996)* showed that addition of a defined amount of water to soil increased the extraction yield of PAH. *Wenclawiak et al. (1992, 1997)* produced extraction results with solvent modified CO_2 that are comparable with soxhlet extraction. Temperature had no influence on the SFE extraction efficiency of PAH *(Langenfeld et al. 1993). Schantz et al. 1997* reported *that* SFE and ASE might produce equivalent or higher yields than soxhlet extraction at lower solvent consumption and shorter extraction time. However, compared to the preceding studies also lower recoveries of SFE were reported indicating that such data are soil composition dependent *(Librando et al. 2004).* Finally, SFE of PAH from soil was compared in an intercomparison of nine laboratories *(Hartonen et al., 2002).* A very good agreement between the laboratories and against soxhlet extraction was obtained demonstrating that reliable results can be obtained by well optimised SFE methods.

- According to *Eschenbach (1994)* and *Codina et al. (1994),* an extraction of soil samples after methanolic saponification increases the yield compared with pure solvent extraction. However, this comparison was carried out against ultrasonication, but not soxhlet extraction *(Eschenbach et al. 1994).*
- *Heemken et al. (1997)* found no significant differences among various PAH extraction methods. Soxhlet extraction, extraction after methanolic saponification, and a ASE and SFE were compared. Ultrasonication alone produced lower yields *(Heemken et al. 1997).* However, sediment and not soil samples were used in these experiments.
- *Shu* and *Lai (2001)* demonstrated that the yield of microwave-assisted extraction is increased and comparable to soxhlet extraction, if the soil sample is remoistened prior to extraction.
- *Chen et al. (1996)* found no differences between various extraction methods including soxhlet extraction and ultrasonication. However, this information should be assessed with caution. In these cases neither the extraction times nor the applied solvents were identical. Such inconsistent comparisons are frequently published.
- *Gfrerer et al. (2002)* compared FBE as a new technique with soxhlet extraction and found comparable yields. FBE can be completed within 1 h. However, the sample load is limited to about 5 g and addition of a porous inert material is needed to obtain the necessary permeability for the solvent (60 mL). Larger sample quantities are desirable to reduce variations due to heterogeneity of the sample.

843 Solvents for extraction

Numerous solvents are recommended for soxhlet extraction in several papers. According to the German *DIN-method 38414, part S20, (1993)* soxhlet extraction uses cyclohexane. Since the studies in the 1970 by Grimmer and co-workers (see *Jacob et al. 1994)* this solvent has frequently been used. Cyclohexane is suitable because clean-up procedure by liquid/liquid extraction may be carried out directly. *Szolar et al. (2002)* found also ethylacetate very convenient, since the extraction of compounds from the sample matrix is reduced.

Jacob et al. (1994) found toluene to be the most suitable solvent. In other studies hexane/acetone *(Schantz et al. 1997),* toluene *(Wenclawiak et al. 1997),* dichloromethane *(Codina et al. 1994)* or dichloromethane/acetone *(Chen et al. 1996)* were used. The last comprehensive solvent comparison with a large variety of difficult matrices (among them soot and sediments) was carried out by *Jonker et al. (2002).* It was found that toluene/methanol (1+6) was superior. However, these solvent mixtures are not suitable for further steps in the clean-up procedure, and the solvent must be exchanged. Since this step always causes losses, this aspect should be considered when designing the method.

Several studies comparing solvents for ASE have also been published. *Zuloaga et al. (2000)* found that chlorinated solvents can be replaced by iso-hexane. A mixture with acetone is of advantage since this solvent supports swelling of the clay structure in soil.

844 Clean-up

When concentrating the extracts, attention should be paid to avoiding losses of 2- and 3-ring PAH. Evaporation to dryness must be strictly avoided and the volume reduction in the rota vapour must never fall below 10 mL. Studies of different volume reduction methods have been published *(Higgings* and *Guerin 1980, Constable et al. 1984, Matthews 1985).*

An alternative clean-up technique may be the treatment of the extract by gel permeation chromatography on Sephadex *(Wenclawiak et al. 1997).* Other examples of clean-up techniques are given in the literature below. However, they have not always been validated and must consequently be carefully examined.

845 Internal standards

High resolution gas chromatography combined with mass spectrometry or flame ionisation allows a complete quality control of each sample by using internal extraction, clean-up and recovery standards. This important quality control measure is not often part of high resolution liquid chromatography, although it would in principle be possible.

Wenclawiak et al. (1992) have shown that 2,2'-binaphthyl is suitable for use as an internal standard. This compound elutes between chrysene and benzo(b)fluoranthene, and may be detected by fluorescence (excitation 270 nm, emission 370 nm).

In an intercalibration exercise, *De Voogt et al. (1996)* asked for an internal standard quantification to be used in HPLC methods. They also proposed indeno(1,2,3-cd)fluoranthene, among other compounds. All the compounds 3,6-dimethylphenanthrene, 2,2'-binaphthyl and indeno-(1,2,3-cd)fluoranthene used as internal standards are not present in real samples.

It is also possible to use isotope-labelled PAH standards. The great advantage is that the recovery of single PAH may be checked accurately. Completely deuterated standards may be separated from the non-labelled PAH by gas chromatography due to the strong isotope effect. However, if chlorinated solvents are used they might cause problems due to deuterium exchange with the sample matrix *(Bolt et al. 1995).* Losses of up to 30 % have been observed. To detect possible losses, a recovery standard should be used whenever using deuterated PAH as an internal standard. For this reason the US EPA has recommended the stable but more expensive ^{13}C-labelled PAH standards.

Moreover, monofluorinated PAH have been suggested as internal standards by *Luthe et al. (2003).* The introduction of one fluorine atom has a small influence on retention time, but does not change the overall chemical and physical properties. They are well-suited for both HRGC and HPLC *(Luthe et al. 2001).* Eight monofluorinated PAH are now commercially available *(Chiron 2004).*

846 Further information

Sander and *Wise (1995)* have summarised important criteria for the selection of HPLC phases for PAH. The temperature dependence of the separation of PAH requires a thermostatisation of the HPLC column *(Maisch 1996, Mäkelä* and *Pyv 1995).* Additional information is also given in the method series of *Agroscope* FAL Reckenholz *(Hort et al. 1998)* and of the *Landesanstalt für Umweltschutz Baden-Württemberg (1992).*

85 Determination of polychlorinated biphenyls (PCB)

851 Preliminary comments

The preferred detection method for PCB is mass spectrometry. For PCBs in complex matrices such as soil, the electron capture detector does not always guarantee the required selectivity. Concentrations that exceed trigger or remediation values must always be confirmed by mass spectrometry.

The literature on PCB analysis contains many methods for its determination in biota and sediments. However, only a few publications deal with the analysis of PCB in soil samples. Furthermore, the methods mentioned often contain identical or similar clean-up steps. The variety of techniques is thus much smaller. As for PAH, the comments below on the single analysis steps of PCB determination are based on practical experience and selected literature.

852 Sample extraction

Most methods are based on soxhlet extraction (e.g. the *Standard DIN 38414, part S20, 1993).* Various extraction methods for PCB in soil were also compared. PCB are considerably less polar than PAH, and consequently the results obtained by different extraction methods deviate much less from each other.

Many of these comparisons were carried out in sediments. These results are also applicable to soils. However, sediments contain a substantially higher fraction of elemental sulphur. Spiked samples were frequently used. *Schantz et al. (1997)* used certified sediment samples. They confirmed that accelerated solvent extraction gives results that are comparable with classical soxhlet extraction.

Levy and *Roselli (1995)* have published a comprehensive summary of the advantages and disadvantages of SFE. *Creutznacher (1998)* found that SFE with CO_2 but without modifier gives results comparable with soxhlet extraction using hexane/acetone 1+1. The results that differ from those for PAH may be explained by the higher lipophilicity of PCB and their lower affinity to the soil matrix (organic substance and clay content).

A disadvantage of SFE is the use of CO_2. Despite its high purity it may still contain lipophilic impurities such as hydrocarbons. At a later clean-up the latter are difficult to remove from PCBs, or cannot be removed at all *(Bernal et al. 1995, Wallace et al 1992).* However, *Pross et al. (2000)* found that CO_2 can be replaced by subcritical water in the same SFE apparatus resulting in comparable recoveries as CO_2 at a much lower price and no risk of contamination.

Enders and *Schwedt (1996)* compared microwave and soxhlet extraction. They found concurring results and mention specifically that the microwave extract contained a much smaller portion of sample matrix.

Peris et al. (2000) found a correlation between organic carbon content of soils and the extraction efficiencies of ultrasonication using European reference soils indicating a risk of systematic errors with this extraction method.

853 Solvents for extraction

In the methods published n-hexane is used almost exclusively as extraction solvent; this may suffice for most soil samples. However, where a very high organic carbon content is present, a more polar solvent such as dichloromethane should be added. The soxhlet extraction according to the German *DIN-method 38414,* part S20 *(1993)* also uses n-hexane. Only occasionally are other solvents used, such as hexane/acetone *(Ayris et al. 1997, Creutznacher 1998)* or pure dichloromethane *(Schantz et al. 1997).*

854 Clean-up

Attention should be paid to minimising PCB losses during volume reduction of extracts. Although losses of PCB 28 to PCB 118 may be considerable, the literature hardly ever mentions this fact. *Chiarenzelli et al. (1996)* pointed to evaporation losses occurring even at room temperature when drying sediments with a high water content. Moreover, without a «keeper» the volume must only be reduced down to about 10 mL.

In most cases, final clean-up is carried out with Florisil (Mg silicate, see *Ayris et al. 1997, Pavoni et al. 1991)* or silica gel *(Creutznacher 1998, Enders* and *Schwedt 1996).* A clean-up using HPLC and a specific activated charcoal may also be possible. The latter allows PCB coeluting on GC phases to be separated *(Böhm et al. 1994). Jang* and *Li (2001)* optimised prefractionation on silica gel, so that PCB and PAH except naphthalene could be obtained in two separate fractions at a shorter time and with less solvent consumption. The remaining naphthalene was present in the PCB fraction.

Validated clean-up methods are part of the *DIN-method 38414,* part S20 *(1993)* and of the *European Standard EN ISO 6468 (1996).* Another method is given in the method series of *Agroscope* FAL Reckenholz *(Hort et al. 1998).*

855 Internal standards

Using internal extraction, clean-up and recovery standards, high-resolution gas chromatography combined with mass spectrometry or electron capture detection makes a complete quality control of each sample possible. It is strongly recommended not to use the external standard method. There is a much higher risk for systematic errors caused by uncompensated matrix effects, and by absence of the recovery control. In this sense the *European Standard EN ISO 6468 (1996)* is a poor example.

Chloronaphthalenes have been proposed as internal standards. They have the same polarity as PCBs and elute in the same fraction. However, interference may occur when using the electron capture detector. Alternatively, PCBs that are not found in real samples may be used.

Luthe et al. (2004) proposed monofluorinated PCB analogue as internal standards. The have nearly the same chemical and physical properties and elute just in front of the parent PCB. In 2004 eight tri- to tetra-monofluorinated PCBs are available among them homologue to PCB 28, 30 and 52 *(Chiron 2004).* More representatives will be synthesised.

However, the best approach is to use ^{13}C-labelled PCBs as internal standards and to determine the individual recoveries in this way.

856 Stationary phases for PCBs

Classic stationary phases for PCB analysis such as 5 % phenyl 95 % polymethylsiloxane (SE-54, DB-5, Ultra 2 etc.) and 14 % cyanopropylphenyl 86 % polymethylsiloxane (OV-1701 etc.) cause problems with certain critical separations such as PCB 28/31 and PCB 138/163. Quite a number of papers that describe improved stationary phases have consequently been published .

At present the carborane high temperature phases HT-5 and HT-8 are the best suited phases. They serve to separate all seven relevant PCBs from interfering congeners *(Böhm et al. 1994, Bøwadt et al. 1994).* The latter paper proposes a combination of stationary phases that separates the seven PCB indicator compounds without any interference. It also mentions complementary papers.

857 Further information

Wells et al. (1992) published recommendations concerning calibration methods in PCB analysis. The procedures proposed by the author also apply to other sectors of micro organic analysis.

86 Determination of polychlorinated dibenzo-*p*-dioxins and dibenzofurans

The *Handbook on Dioxins (Oehme 1998)* contains a comprehensive chapter on the analysis and quality control of these compounds; it also covers soil analysis. This book, which also lists important papers up to the year 1998, is referenced below.

During the past years the methodological progress was concentrated on more time-efficient extraction and clean-up procedures. However, no principally new technique were introduced. Therefore, only a brief update is necessary concentrating mainly on extraction procedures.

ASE has also become popular in dioxin analysis in soil. *Preud'homme* and *Potin-Gautier (2003)* have optimised its parameters and found that extraction was comparable with soxhlet extraction and complete within 15 min at 130 °C. However, *Henkelmann et al. (1999)* had to use a higher temperature of 185 °C and at least four cycles of 10 min each to reach a complete extraction of the isotope-labelled internal standards. Extraction of the native compounds were complete after 2 cycles.

Mannilia et al. (2002) could show that also SFE allows to obtain similar extraction efficiencies as soxhlet with CO_2 only. A trap containing a mixture of activated charcoal and cellite was used allowing a clean-up step directly after extraction. However, *Fiddler et al. (2000)* found that PCDD/PCDF may be formed from chlorophenol containing solids, if SFE is used.

9 Bibliography

91 Papers on the quality assurance concept

- Ambidge P.F., Cox E.A., Creaser C.S., Greenberg M., Gem M.G., Gilbert J., Jones P.W., Kibblewhite M.G., Levey J., Lisseter S.G., Meredith T.J., Smith L., Smith P., Startin J.R., Stenhouse I. and Whitworth M., 1990, Acceptance criteria for analytical data on polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans, Chemosphere, 21, 999.
- Barwick V J, Ellison S.L.R, 2000, Protocol for uncertainty evaluation from validation data, VAM Project, LGC/VAM/1998/088, *http://www.vam.org.uk/*
- DIN Deutsches Institut für Normung e.V., 1999, Leitfaden zur Angabe der Unsicherheit beim Messen; Deutsche Fassung ENV 13005, 1999, Herausgeber: Beuth Verlag GmbH, Berlin-Wien-Zürich.
- DIN EN ISO/IEC 17025, 2000, Allgemeine Anforderungen an die Kompetenz von Prüf- und Kalibrierlaboratorien, Herausgeber: DIN Deutsches Institut für Normung e.V., Beuth Verlag GmbH, Berlin-Wien-Zürich.
- EURACHEM/CITAG Guide CG4, 2000, Quantifying uncertainty in analytical measurement. Second edition. ISBN 0 948926 15 5.
- Eurolab Technical Report No. 1, 2002, Measurement Uncertainty in Testing, *http://www.eurolab.org/.*
- European Accreditation (EA) document EA-4/02, 1999, Expressions of the Uncertainty of Measurements in Calibration. (previously EAL-R2), *http://www.european-accreditation.org/.*
- European Standard EN 1948-1,2,3, 2004, Determination of Mass concentration of PCDD/PCDF. European Committee for Standardization, Central Secretariat, Rue de Stassart 36, B-1050 Brussels, Belgium
- Günzler, 1994, Akkreditierung und Qualitätssicherung in der analytischen Chemie, Springer Verlag Heidelberg, ISBN 3-540-58136-7.
- International Organization for Standardization, 1995, Guide to the Expression of Uncertainty in Measurement. (GUM), corrected and reprinted 1995, Geneva, Switzerland.
- International Organization for Standardization (ISO), 1998, ISO17025, General Requirements for the Competence of Testing and Calibration Laboratories, Geneva, Switzerland..
- International Organization for Standardization, ISO/DTS 21748, 2003, Guide to the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation, Geneva, Switzerland.
- Nordtest Technical Report 537, 2003, Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories, *http://www.nordtest.org/*
- Quevauvillier Ph. (ed.), 1995, Quality assurance in environmental monitoring, sampling and sample pretreatment, VCH Weinheim.
- Subramananian G. (ed.), 1995, Quality assurance in environmental monitoring, instrumental methods, VCH Weinheim.
- SAEFL (Swiss Agency for the Environment, Forests and Landscape), 2003, Sampling and sample pretreatment for soil pollutant monitoring – Manual, 87 p., Berne.
- Swiss Federal Council, Ordinance of 1^{s} July 1998 relating to impacts on the soil (OIS; SR 814.12).

92 Papers on chapter 8 of the present guidelines

- Ayris S., Currado G.M., Smith D. and Harrad S., 1997, GC/MS procedures for the determination of PCBs in environmental samples, Chemosphere, 35, 905.
- Bernal J.L., Jimenez J.J. and Rivera J.M., 1995, Interferences found in the determination of pesticide and PCB residues by capillary GC after SFE, J.Chromatogr. Sci., 33, 500.
- Böhm V., Schulte E. and Thier H.-P., 1994, Carbon column HPLC and carborane-phase capillary GLC for the separation of polychlorinated biphenyl congeners, Fresenius J.Anal.Chem., 348, 297.
- Bolt D.L., Bradley J.C. and Re M.A., 1995, The preparation of ^{13}C-labeled standards of polycyclic aromatic hydrocarbons and other micropollutants: Synthetic and QA/QC considerations, Organohalogen Compounds., 23, 255.
- Bøwadt S., Skejø-Andresen H., Montanarella L. and Larsen B., 1994, HRGC-Separation of 160 chlorobiphenyls in technical mixtures on four polar narrow-bore columns, Intern. J.Environ.Anal.Chem., 56, 87.

- Chen C.S., Rao P.S.C. and Lee L.S., 1996, Evaluation and detection methods for determining polynuclear aromatic hydrocarbons from coal tar contaminated soils, Chemosphere, 32, 1123.
- Chiarenzelli J., Scrudato R., Arnold G., Wunderlich M. and Rafferty D., 1996, Volatilization of polychlorinated biphenyls from sediment during drying at ambient conditions, Chemosphere, 33, 899.
- Chiron AS, Stiklestadveien 1, N-7041 Trondheim, Norway, www.chiron.no
- Codina G., Vaquero M.T., Comellas L. and Broto-Puig F., 1994, Comparison of various extraction and clean-up methods for the determination of polycyclic aromatic hydrocarbons in sewage sludge-amended soils, J.Chromatogr. A., 673, 21.
- Constable D.J.C., Smith R.S. and Tanaka J., 1984, Comparison of solvent reduction methods for concentration of polycyclic aromatic hydrocarbon solutions, Environ.Sci.Technol., 18, 975.
- Creutznacher H., March 1998, Neue Extraktionstechniken in der organischen Umweltanalytik (Teil 2), GIT Laborfachzeitschrift, 277.
- De Voogt P., Hinschberger J., Maier E.A., Griepink B., Muntau H. and Jacob J., 1996, Improvements in the determination of eight polycyclic aromatic hydrocarbons through a stepwise interlaboratory study approach, Fresenius J.Anal.Chem., 356, 41.
- DIN 38414, part S20, 1993, German standard methods for the examination of water, waste water and sludge – Sludge and sediments (group S), Determination of 6 polychlorinated biphenyls (PCB), Draft October 1993.
- Enders B. and Schwedt G., March 1996, Mikrowellenunterstützte Extraktion in der Analytik von PCB und PAK aus Boden und Klärschlamm, GIT Laborfachzeitschrift, 172.
- Eschenbach A., Kästner M., Bierl R., Schaefer G. and Mahro B., 1994, Evaluation of a new effective method to extract polycyclic aromatic hydrocarbons from soil samples, Chemosphere, 28, 683.
- European Standard EN ISO 6468, 1996, Water quality – Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes, European Committee for Standardization, rue de Stassart 36, B-1050 Brussels.
- Fiddler W., Pensabene J.W., Shadwell R.J. and Lehotay S.J., 2000, Potential artifact formation of dioxins in ball clay during supercritical fluid extraction, J.Chromatogr. A, 902, 427.
- Gfrerer M., Serschen M. and Lankmayr E., 2002, Optimized extraction of polycyclic aromatic hydrocarbons from contaminated soil samples, J.Biochem Biophys Methods, 53, 203.
- Goerlitz D.F. and Law L.H., 1971, Note on removal of sulfur interferences from sediment extracts for pesticide analysis, Bull.Environ.Cont.Toxicol., 6, 9.
- Hartonen K., Bøwadt S., Dybdahl H.P., Nylund K., Sporring S., Lund H. and Oreld F., 2002, Nordic laboratory intercomparison of SFE for the determination of total petroleum hydrocarbon, polychlorinated biphenyls and polycyclic aromatic hydrocarbons in soil, J.Chromatogr. A, 958, 239.
- Heemken O.P., Theobald N. and Wenclawiak B.W., 1997, Comparison of ASE and SFE with Soxhlet, sonication and methanolic saponification extractions for the determination of organic micropollutants in marine particulate matter, Anal.Chem., 69, 2171.
- Henkelmann B., Wottgen T., Chen G., Schramm K-W. and Kettrup A., 1999, Accelerated solvent extraction of different matrices in the analysis of PCDD and PCDF: Method development and comparison to soxhlet extraction, Organohalogen Compd., 40, 133.
- Higgins C.E. and Guerin M.R., 1980, Recovery of naphthalene during evaporative concentration, Anal.Chem., 52, p. 1984.
- Hort R., Gupta S. and Häni H., 1998, Methodenbuch für Boden-, Pflanzen- und Lysimeterwasser-Untersuchungen, Schriftenreihe FAL Nr. 27, Agroscope FAL, Zürich-Reckenholz.
- Jacob J., Grimmer G., Hanssen H-P. and Hildebrand A., 1994, Extractability and bioavailability of PAH from soil and air particulate matter, Polycyclic Arom.Compd., 5, 209.
- Jang J-K. and Li A., 2001, Separation of PCBs and PAHs in sediment samples using silica gel fractionation chromatography, Chemosphere, 44, 1439.
- Jensen S., Renberg L. and Reuthergård L., 1977, Residue analysis of sediment and sewage sludge for organochlorines in the presence of elemental sulfur, Anal.Chem., 49, 316.
- Johansen J.E., Luthe G., Leonhards P. and Liu H., Monofluorinated analogues of polychlorinated biphenyls (F-PCBs) - standards for analysis: retention behaviour in gas chromatography and MS characteristics, 2004, Organohalogen Compd. 66, 201.
- Jonker M.T.O.and Koelmans A.A., 2002, Extrtaction of polycyclic aromatic hydrocarbons from soot and sediment: Solvent evaluation and implications to sorption mechanisms, Environ.Sci.Technol., 36, 4107.

- Landesanstalt für Umweltschutz Baden-Württemberg, 1992, Richtlinie zur Bestimmung von polycyclischen aromatischen Kohlenwasserstoffen (PAK) in Boden-, Abfall- und Altlastenproben, LfU State Institute for Environmental Protection, Karlsruhe.
- Langenfeld J.J., Hawthorne S.B., Müller D.J. and Pawliszyn J., 1993, Effects of temperature and pressure on SFE efficiencies on polycyclic aromatic hydrocarbons and polychlorinated biphenyls, Anal.Chem., 65, 338.
- Leonhardt E. and Stahl R., 1998, Decomposition of acenaphthylene by ultrasonic irradiation, Anal.Chem., 70, 1228.
- Levy J.M. and Rosselli A.C., 1995, Current status of supercritical fluid extraction in environmental analysis, in: G. Subramaniam (ed.), Quality assurance in environmental monitoring, Instrumental methods, VCH, Weinheim.
- Librando V., Hutzinger O., Tringali G. and Aresta M., 2004, Supercritical fluid extraction of polycyclic aromatic hydrocarbons from marine sediments and soil samples, Chemosphere, 54, 1189.
- Luthe G., Broeders J., Brinkman U.A.Th., 2001, Monofluorinated polycyclic aromatic hydrocarbons as internal standards to monitor trace enrichement and desorption of their parent compounds during solid-phase extraction, J.Chromatogr. A, 933, 27.
- Luthe G., Ramos L., Dallge J., Brinkman U.A.Th., 2003, Monofluorinated analogues of polycyclic aromatic hydrocarbons as internal standards for GC-MS in environmental analysis, 2003, Chromatographia, 57, 379.
- Maisch A., 1996, Vorschriftsgemässe PAK-Messungen, LaborPraxis, Juli/August, 40.
- Mäkelä M. and Pyv L., 1995, Effect of temperature on retention time reproducibility and on the use of programable fluorescence detection of fifteen polycyclic aromatic hydrocarbons, J.Chromatogr. A., 699, 49.
- Mannila M., Kiostine J. and Vartianen T., 2002, Development of supercritical fluid extraction with a solid pahse trapping for fast estimation of toxic load of polychlorinated dibenzo-p-dioxins-dibenzofurans in sawmill soil, J.Chromatogr. A, 975, 189.
- Matthews E.W., 1985, Recovery of dichlorobenzenes, nitrobenzene, and naphthalene during evaporative concentration, Anal.Chem., 57, 1494.
- Oehme M., 1998, Analytik und Qualitätssicherung der Dioxinbestimmung, in: Oehme M. (ed.), Handbuch Dioxine, Kapitel 3, Spektrum Akademischer Verlag, Heidelberg.
- OSBO, Arbeitsgruppe «Organische Schadstoffe im Boden (OSBO)», 1997, Untersuchungen zur Standardisierung des Vorgehens bei der Bestimmung von polyzyklischen aromatischen Kohlenwasserstoffen im Boden, Sulzer Innotec, Winterthur.
- Pavoni B., Sfriso A. and Raccanelli S., 1991, Quantification of PCBs in environmental samples: Comparison of results obtained with different analytical instruments (GC-ECD, GC-MS) and standards, Intern. J.Environ. Anal.Chem., 44, 11.
- Peris, N., Vasilic Z., Fingler S. and Drevenkar V., 2000, Trace enrichment of polychlorinated biphenyls in soil: efficiency of sonicated liquid-solid extraction with acetone-n-Hexane mixture from different soil types, Croatica Chemica Acta, 73, 229.
- Preud'homme H. and Potin-Gautier M., 2003, Optimization of accelerated solvent extraction for polyhalaogenated dibenzo-p-dioxins and benzo-p-furans in mineral and environmental matrixes using experimental designs, Anal.Chem. 75, 6109.
- Pross S., Gau W. and Wenclawiak B.W., 2000, Extraction of polychlorinated biphenyls with supercritical carbon dioxide, sulfur hexafluoride and subcritical water, Fresenius J.Anal.Chem. 367, 89.
- Sander L.C. and Wise S.A., 1995, Retention and selectivity for polycyclic aromatic hydrocarbons in reversed phase liquid chromatography, in: R.M. Smith (ed.), Retention and selectivity in liquid chromatography, J.Chromatogr.Library, 57, 337.
- Schantz M.M., Nichols J.J. and Wise S.A., 1997, Evaluation of pressurized fluid extraction for the extraction of environmental matrix reference materials, Anal.Chem., 69, 4210.
- Schleussinger A., Ohlmeier B., Reiss, I. and Schulz S., 1996, Moisture effect on the clean-up of PAH-contaminated soil with dense carbon dioxide, Environ.Sci.Technol., 30, 3199.
- Shu Y.Y. and Lai T.L., 2001, Effect of moisture on the extraction efficieny of polycyclic aromatic hydrocharbons from soils under atmospheric pressure by focused microwave assisted extraction, J. Chromatogr. A, 927, 131.
- Song Y.F., Jing X., Fleischmann S. and Wilke B.-M., 2002, Comparative study of extraction methods for the determination of PAHs from contaminated soils and sediments, Chemosphere, 48, 993.
- Szolar O.H.J., Rost, H., Braun R. and Loibner A.P., 2002, Analysis of polycyclic aromatic hydrocarbons in soil: Minimizing sample pretreatment using automated soxhlet with ethyl acetate as extraction solvent, Anal. Chem., 74, 2379.

- Wallace J.C., Krieger M.S. and Hites R.A., 1992, Reduction of contamination levels in on-line supercritical fluid extraction systems, Anal.Chem., 64, 2655.
- Wells D.E., Maier E.A. and Griepink B., 1992, Calibrants and calibration for chlorobiphenyl analysis, Intern. J.Environ.Anal.Chem., 46, 255.
- Wenclawiak B., Rathmann C. and Teuber A., 1992, Supercritical fluid extraction of soil samples and determination of polycyclic aromatic hydrocarbons (PAHs) by HPLC, Fresenius J.Anal.Chem., 344, 497.
- Wenclawiak B.W., Paschke T. and Krappe M., 1997, Supercritical fluid extraction of polycyclic aromatic hydrocarbons from native soil and fly ash with pure and modified carbon dioxide and dimethylether, Fresenius J.Anal.Chem., 357, 1128.
- Zuloaga O., Fitzpatrick L.J., Etxebarria N. and Dean J.R., 2000, Influence of solvent and soil type on the pressurised fluid extraction of PAHs, J.Environ.Monit., <u>2</u>, 634.