Review

Improvement of quality control of speciation analysis using hyphenated techniques
A decade of progress within the European Community

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Abstract

The awareness of a need for an improved control of environmental contamination levels has led to the development of new hyphenated techniques for the determination of a wide variety of chemical species (e.g., organotins, methyl-mercury, alkyl-lead compounds etc.). These techniques generally involve many analytical steps such as extraction, derivatisation, separation and detection which have to be carried out in such a way that the speciation is not changed during the analytical process. The need for evaluating the method's performance has led the BCR programme of the European Commission (now Standards, Measurements and Testing Programme) to conduct series of interlaboratory studies during the last decade. These projects followed a step-by-step approach for the evaluation of different steps of the analytical methods used, e.g., simple solutions to test the detection, cleaned extract to evaluate the separation, spiked samples to test the extraction and natural samples to evaluate the whole analytical procedures. These collaborative projects allowed most of the sources of errors related to either a technique or a laboratory to be detected and removed. This paper gives an account of discussions of possible errors occurring in speciation analysis and presents examples of technical scrutiny of hyphenated techniques using chromatography as applied to the determination of tributyltin, methyl-mercury and trimethyllead.

Keywords: Reviews; Environmental analysis; Speciation; Organotin compounds; Organolead compounds; Organomercury compounds

Contents

1. Introduction

The development of hyphenated techniques using chromatography for speciation analysis has found many applications within the past ten years, e.g., for the monitoring of toxic organometallic compounds such as tributyltin (TBT) and methyl-mercury. The determination of a series of chemical species, known as speciation analysis, is nowadays performed routinely in many laboratories to control the quality of the environment, food and health. It was soon recognised that the need for comparability of data produced worldwide requires that the analyses are accurate; this can be achieved in a collaborative way by systematically comparing analytical methods. Therefore, in order to improve and ensure a good quality control of speciation analysis, the Community Bureau of Reference, BCR (now Standards, Measurements and Testing Programme) of the European Commission (DG XII) has organised a series of interlaboratory projects over the last decade as well as the production of certified reference materials (CRMs). The state of the art of speciation analysis has also been discussed in the frame of two BCR-workshops held, respectively, in Arcachon (France) in 1990 [1] and Rome in 1994 [2,3]. Discussions enabled the identification of sources of errors occurring at different steps and the proposal of solutions for the errors.

This paper gives a summary of the expert's discussion on the sources of errors possibly occurring in speciation analysis and presents an overview of projects in which hyphenated techniques were evaluated.

2. The SM&T programme — role and action

The harmonisation of measurement methodologies is a continuous process which may be facilitated either by means of EC Directives or the establishment of Norms (e.g., ISO or CEN standards). However, the measurements and analyses required for the implementation of these Norms and Directives are sometimes so difficult that, even when applying the same method, laboratories may still obtain very different results. Such disagreement between lab-oratories prevents the regulations being respected. The regulations therefore have no harmonisation effects. In order to eliminate disputes arising from doubtful measurements, the European Commission established the Community Bureau of Reference (BCR) more than 20 years ago (in 1973) to support technical collaboration between laboratories of the EC Member States. In this way, the Community helped laboratories in the Member States to provide reliable measurements in those sectors which are vital to the Community, i.e., trade, agriculture, food, industrial products, environment, health and consumer protection. To pursue this action, the European Commission implemented the Standards, Measurements and Testing (SM&T) Programme (1994–1998). By addressing the issues highlighted above, this programme aims to contribute to the harmonisation and improvement of methods of measurement and analysis when these methods are not sufficiently accurate and laboratories obtain different results. In practice, where the action of the BCR was limited to the organisation of interlaboratory studies and production of CRMs, the SM&T Programme now expands this activity to the technical support necessary for the development and application of EC policies (internal market, environment, agriculture, health etc.) and development of the measurement infrastructure of Europe. Besides the continuation of the classical BCR work, the programme is presently supporting the development of new methods of measurements and pre-normative research (in support of activities of normative bodies, e.g., CEN).

One of the major tasks of the SM&T Programme essentially consists of organising projects in which participating laboratories may collaborate to improve the measurement or analysis concerned. With regards to speciation analysis, this type of project enabled the evaluation of various hyphenated techniques, using a stepwise approach of at least two major phases:

2.1. Step by step approach

Hyphenated techniques used for the determination of chemical forms of elements are based on successive steps which may vary from one procedure to another. As discussed below, methods have their

own particular source of error. For instance, for some techniques such as gas chromatography (GC), errors may occur due to e.g., an incomplete derivatisation, a step which is not necessary for other techniques such as high-performance liquid chromatography (HPLC); the latter technique, however, may have errors such as incomplete separation which is not encountered, or to a lesser extent, in the former technique. An independent method should be used to verify the results of routine analysis. If the results of both methods are in good agreement, it can be concluded that the results of the routine analysis are unlikely to be affected by a contribution of systematic nature (e.g., insufficient extraction). This conclusion is stronger when the two methods differ widely, such as derivatisation–GC–atomic absorption spectrometry (AAS) and HPLC–inductively coupled plasma mass spectrometry (ICP-MS). If the methods have similarities, such as an extraction step, a comparison of the results will most likely lead to conclusions concerning the accuracy of the method of final determination, and not as regards the analytical result as a whole. Interlaboratory studies are therefore valuable tools to evaluate analytical techniques [4]; in particular, a good procedure to evaluate the performance of hyphenated (multi-step) techniques is to separately examine the different steps and evaluate the sources of error which may arise. To do so, different samples, previously characterised by their homogeneity and stability, are prepared and sent to the participating laboratories. Typical matrices are:

1. Solutions containing one or several pure analytes including potential interfering compounds to evaluate the performance of the final detection and of the separation techniques.
2. Cleaned extracts to test the performance of the separation.
3. Raw extracts to verify the clean-up procedure.
4. Real matrices homogeneously enriched and equilibrised with the analyte(s) to be determined to test the total analytical procedure.
5. Real samples.

This evaluation enables the identification of the sources of error at each analytical step and consequently help the laboratories to remove them.

2.2. Certification

Results can only be accurate and comparable worldwide if they are traceable. By definition, traceability of a measurement is achieved by an unbroken chain of calibrations connecting the measurement process to the fundamental units. In the vast majority of chemical analyses, the chain is broken because the treatment involves destruction of the sample by dissolution, calcination, etc. To approach full traceability it is necessary to demonstrate that no loss or contamination has occurred in the course of the sample treatment; in the case of speciation analysis, it should also be verified that the chemical species have been preserved. The only possible way for any laboratory to ensure traceability in a simple manner is to verify the analytical procedure by means of a so-called matrix reference material (RM) certified in a reliable manner. The laboratory which measures such an RM by its own procedure and finds a value in disagreement with the certified value is thus warned that its measurement includes error(s) the source of which must be identified. Thus, CRMs having well known properties should be used to:

1. verify the accuracy of results obtained in a laboratory;
2. monitor the performance of the method (e.g., cusum control charts);
3. calibrate equipment which requires a calibrant similar to the matrix, e.g., optical emission spectrometry, X-ray fluorescence (XRF) spectrometry;
4. demonstrate equivalence between methods;
5. detect errors in the application of standardised methods (e.g., ISO, ASTM, etc.).

The conclusion on the accuracy obtained on the unknown sample is always a conservative one: if the laboratory finds wrong results on a CRM it is by no means certain of a good performance on the unknown. If, however, the laboratory finds a value in agreement with the certified value, it should realise that owing to discrepancies in composition between CRM and unknown, there is a risk that the result on the unknown may be wrong. The use of as many as possible relevant CRMs is therefore necessary for good quality assurance (QA). The CRMs produced

are as close as possible as real matrices to match the analytical difficulties encountered in the analyses of environmental samples. Besides its role of a method's performance evaluation, a CRM as prepared by the BCR can thus be considered as a material which disseminates the experience collected by those laboratories who improved the quality of their measurements in a number of intercomparisons and demonstrated their accuracy [4].

3. Sources of errors occurring in speciation analysis

Hyphenated techniques for speciation analysis were developed in the early 1980's. These techniques generally involve several analytical steps, i.e., extraction either with organic solvents (e.g., toluene, dichloromethane) or different types of acids (e.g., acetic or hydrochloric acid), derivatisation procedures (e.g., hydride generation, ethylation), separation steps (GC or HPLC) followed by a detection of the compound or the element by a wide variety of methods, e.g., AAS, ICP, MS, flame photometric detection (FPD), flame ionisation detection (FID), electron-capture detection (ECD), etc. Each step of the analytical procedure includes specific sources of error as discussed below (the examples have been taken from the summary of round-tables of the workshops on speciation mentioned in the introduction [1–3]); basically all steps should be carried out in such a way that the analyte is separated from the interfering matrix without loss or contamination, nor changes of the speciation.

3.1. Extraction

A wide variety of acid extraction procedures have been used for sediment and biota analyses particularly when AAS is used as the final determination step; these involved acids such as hydrochloric acid, acetic acid, hydrochloric–acetic acid mixture, etc., for organotin compounds [5–7]. Other procedures, e.g., for techniques involving GC or HPLC, are based on extraction with an organic solvent, e.g., dichloromethane, chloroform, toluene, hexane, etc. [8–10].

Good quality control implies that the extraction

recoveries are verified; this can be done by spiking a sample of similar composition as the sample analysed with a known content of the analyte concerned, leaving it to equilibrate and determining the analyte after extraction. The major drawback is that the spike is not always bound the same way as the naturally occurring compounds. Alternatively, and only if the extraction procedure does not change the matrix composition and appearance, the recovery experiment may be carried out on the previously extracted real sample by spiking, equilibration and extraction. However, the recovery assessment can often be overestimated and this risk should be faced; CRMs may be a tool to ascertain accuracy; they are, however, only useful in cases where they contain integral, and not spiked, species.

Spiking experiments are particularly important although not without their problems. Participants in the speciation workshops [1–3] agreed that although the present knowledge is not perfect, the use of spiking experiments helps to minimise errors (a technique which does not give good results with a spiked sample will not be applicable to natural samples; the reverse is not systematically true, i.e., a technique with a good spike recovery may give poor results in the extraction of integral compounds). A general agreement in the workshop discussions underlined the convenience of checking extraction efficiency at least in duplicate extraction experiments over the same sample.

Extraction recoveries may vary from one chemical species of the same metal to another and they should, consequently, be assessed independently for each compound as well as for the compounds together. A compromise has also to be found between a good recovery (sufficiently strong attack) and the preservation of the speciation.

For a thorough evaluation of extraction methods, materials with an integral analyte (i.e., bound to the matrix in the same way as the unknown) which is preferably labelled (radioactive labelling would allow to verify the recovery) would be necessary. Such materials not being available the extraction method used should be validated by other independent methods.

Supercritical fluid extraction methods are quite promising in this respect. Such methods are currently being developed e.g., for butyltins [11] and seem to

offer good possibilities for extracting the species without alteration.

3.2. Derivatisation

Derivatisation procedures may be used to separate trace elements from their matrices and to concentrate the analyte species, i.e., to generate species which are more easily separated from each other by chromatography. Reactions employed nowadays are mostly centred around the addition of simple groups, e.g., alkylation with Grignard reagents (e.g., ethylation, butylation, pentylation).

Hydride generation (carried out in acid media) generally uses sodium borohydride as reductant and hydride transfer agent to yield metal and metalloid hydrides. The main advantage of this reaction is that metal-carbon cleavage does not occur and the speciation is therefore maintained. A wide range of element-species can be determined using this approach such as As, Ge, Sb, Se and Sn. By selecting a proper pH in the reaction vessel the range of compounds that yield hydrides is restricted. However, hydride generation cannot be applied to the determination of some organic compounds, e.g., arsenobetaine [12] (unless the molecule is first destroyed by UV-irradiation) and the reaction can be inhibited in the presence of high contents of organic compounds in the matrix as shown for butyltins [13].

Grignard reactions, e.g., pentylation, are widely used for the determination of alkyl-Pb and Sn species; the reaction yields products which can be separated relatively easily by GC. In some cases, e.g., for alkyl-Pb species [14], a back-extraction is necessary, which increases the risks of contamination or losses. In addition, the verification of the yield of derivatisation is presently hampered by the lack of suitable calibrants.

The use of sodium tetraethylborate overcomes the problem of hydrolytic instability of the Grignard reagents, allowing ethylation to be carried out in an aqueous medium. This reaction has been employed for the analysis of alkyl-Pb, Sn and Hg species [15,16].

At present, derivatisation reactions are far from being well controlled. Despite the many publications, the reaction mechanisms of derivatisation are not well understood which certainly holds also for

hydride generation procedures. In general, the risk of producing a wrong result increases with the number of steps and with their complexity in a determination. Therefore, if derivatisation can be avoided it is worthwhile considering such possibility.

The workshop discussions in Rome [2,3] highlighted several major problem areas:

1. derivatisation yields, being often matrix dependent, are difficult to determine due to the lack of appropriate, high purity calibrants;
2. the increased number of analytical steps prior to and after derivatisation (such as extraction, preconcentration and clean-up) increase the overall uncertainty;
3. the stability of some derivatives is poor and may be affected by uncontrollable factors, such as the initial sample composition.

Recommendations for improving this situation were given and can be found in the summary of round-table discussions [2].

3.3. Separation

The separation of chemical species of elements can only be performed by techniques which do not destroy the chemical forms. Classical techniques used so far were: GC (packed or capillary), cold trapping (U-tube filled with chromatographic material) and liquid chromatography (LC).

GC has become a powerful tool in the determination of traces of organic compounds. Unfortunately, such developments are not sufficiently applied in speciation analysis. Whereas for most environmental applications packed columns are abandoned for the determination of traces of organic compounds because of poor separation and time-consuming procedures, they are still widely used for speciation, e.g., for methyl-mercury determinations as well as for butyltins (packed GC in a U-tube).

As in organic analysis, precautions should be taken to preserve the compound integrity in the column. For example in GC-separation of Sn species, a heat-induced decay may occur leading to the deposition of Sn oxides in the capillary column which in turn cause peak tailing.

Thermostable and volatile compounds may be separated by GC. Several stationary phases are available on fused-silica capillary columns. The separation power relies on the polarity of the compounds and of the stationary phase. This separation method often requires a derivatisation step.

For LC (e.g., HPLC) systems there is no need for derivatisation prior to separation. Unfortunately, stationary phases in HPLC are less commonly used (e.g., ion-exchangers, ion pairing) than in GC; consequently, separation problems may still exist for some species (e.g., As-betaine/As(III)). However, LC is better suited for element specific detections such as ICP-AES or ICP-MS, AAS, XRF, neutron activation analysis (NAA) or electrochemical detectors.

Cold trapping has been used successfully for the determination of e.g., alkyl-Sn and Se compounds [17], Pb and some As compounds [18]. The technique presents both advantages to concentrate the species and to sequentially separate them according to their specific volatility. One drawback of this method is that only volatile forms of elements (hydrides, ethylated or methylated forms) may be separated; other molecules of low volatility, e.g., TPhT, As-betaine etc., cannot be separated. In addition, cold trapping requires a derivatisation step. Both steps are difficult to validate and it is still unclear which physical and chemical parameters may hamper, for a given matrix, the formation and separation of volatile forms. Although the technique is not always applicable, its simplicity and the fact that it can operate on-line with derivatisation steps makes it a recommended method for a variety of compounds.

Within the Rome workshop discussions, there appeared to be general agreement within the group that liquid separation techniques offered more potential than gaseous separation methods. A much greater range of analytes can, in principle be separated by the liquid separation methods. Problems, however, still exist with the stability of silica based ion-exchange columns. With regard to capillary gas chromatography, the group concluded that the problems experienced with capillary column gas chromatography were generally the same as those encountered in trace organic analysis.

3.4. Detection

The detectors used for speciation analysis are either element specific (e.g., AAS) or non specific (e.g., FID, FPD, ECD). In general, the determinant should arrive alone into the detector to avoid interferences; multi-component detection (e.g., ICP-AES, ICP-MS, NAA) may have larger uncertainties. In speciation analysis, the choice of the detector strongly depends on the chemical forms to be determined and on the mode of separation used.

Electrothermal AAS (ETAAS), although being a sensitive technique, is generally not recommended for speciation analysis, as the method cannot be applied in a continuous (on-line) mode. The necessary manipulations, caused by the off-line character of the method, increase the risks of errors considerably.

Whenever applied, the precautions for the measurement are the same as for inorganic analysis; the choice of the matrix modifier, the temperature programme, etc., should follow the same rules as for the determination of the element content.

Flame or quarts furnace AAS are often used as an element-sensitive detector. When various parameters are chosen and set properly, the technique can be performed on-line; provided that a proper separation (e.g., GC, cold trapping) is achieved it can be used to determine the various species containing the same element.

ICP-AES or ICP-MS can be used on-line after HPLC separation, using a proper interface. MS can be specific in certain cases and even would allow an on-line QA in the isotope dilution mode.

Classical detectors after LC or GC separation may be applied for the determination of some chemical forms of elements e.g., FPD or FID detection for TBT.

4. Examples of evaluation of hyphenated techniques

This section gives an account of projects in which hyphenated techniques using chromatography were evaluated in the frame of collaborative projects

organised by BCR-programme (now SM&T programme).

4.1. Determination of trimethyllead

Trimethyllead is currently determined to monitor atmospheric contamination. A project has started in 1990, aiming to organise an intercomparison on solutions of pure trimethyllead. The stability of this compound in solution and the feasibility of preparation of samples for the intercomparisons have been investigated in 1990–1992 [19] and a first exercise on trimethyllead in solutions was successfully concluded in 1993 [20]. A further development has focused on the preparation of artificial rainwater and urban dust for a second interlaboratory study on trimethyllead, of which the results were discussed in 1994 [21]. Candidate reference materials of artificial rainwater and urban dust were prepared in 1995 and certification is planned for the second half of 1996; calibrants of verified purity and stoichiometry will also be distributed to the participants, along with an urban dust sample spiked with trimethyllead for recovery experiments. A separate project was carried out to develop a HPLC–ID–ICP-MS method for Pb-speciation which could be used in the certification [22].

Hyphenated techniques evaluated in this project were the following:

1. Diethyldithiocarbamate complexation with EDTA–hexane; ethylation (with $NaBEt_4$); hexane extraction; capillary GC separation and detection by microwave induced plasma atomic emission spectrometry.
2. Diphenylthiocarbazone extraction in dichloromethane–hexane; Grignard reaction (butylation with butylmagnesium chloride); packed GC separation (cryogenic trapping) and detection by quartz furnace (T-tube) AAS.
3. Addition of NaCl; ethylation (with $NaBEt_4$); packed GC separation (cryogenic trapping) and detection by quartz furnace (T-tube) atomic absorption spectrometry.
4. Diethyldithiocarbamate complexation and pentane extraction; Grignard reaction (butylation with butylmagnesium chloride); capillary GC separa-

tion and detection by graphite furnace atomic absorption spectrometry.

The other techniques used in the project were based on electrothermal atomic absorption spectrometry (no chromatographic separation), differential pulse anodic stripping voltammetry and ICP-MS after ion-exchange.

All techniques gave satisfactory results and were considered to be suitable for use in the trimethyllead certification.

4.2. Determination of methyl-mercury

Methyl-mercury (MeHg) is known to accumulate in the food chain and to have highly toxic effects on biota and humans. A project to improve the quality of MeHg determination in Europe started within the BCR-programme some years ago, involving interlaboratory studies of solutions of pure analytes and fish extracts [22]. The results of the second round-robin exercise on extracts revealed a high dispersion of results and the presence of uncontrolled sources of error; it was therefore decided to perform a third intercomparison with other fish extracts to remove the remaining bias, particularly those apparently due to the use of GC packed columns. Mussel and tuna samples were also analysed to evaluate the long term reproducibility of methods. These exercises were successfully concluded and the results obtained allowed the organisation of a certification campaign of two tuna fish materials (with low and high levels of MeHg) which was conducted in 1992–1993 [23]. The CRMs 463 and 464 are currently available [24].

The efforts to improve the quality control of MeHg determination in the environment are now continuing in the frame of an M&T project which aims to certify the contents of MeHg in a freshwater or lagoon sediment. An interlaboratory study has enabled the evaluation of the techniques on a highly contaminated sediment [25]; the results were encouraging enough to start a certification campaign which was successfully concluded in 1996 [26].

Hyphenated techniques using chromatography which were evaluated in the frame of this project were:

1. Westöö extraction (HCl–toluene–cysteine acetate–toluene); capillary GC–ECD.
2. HCl addition–clean-up with acetone and toluene extraction; capillary GC–ECD.
3. Acetic–sulphuric acid extraction; headspace GC separation followed by atomic fluorescence spectrometric detection.
4. Addition of hydrochloric–sulphuric acid–toluene extraction; $NaBH_4$ derivatisation; capillary GC separation and detection by Fourier transformation infrared spectroscopy.
5. Addition of NaCl; leaching with HCl followed by NaOH neutralisation; diethyldithiocarbamate–toluene extraction; butylation with Grignard reagent (butylmagnesium chloride); capillary GC separation and detection by microwave induced plasma atomic emission spectrometry.
6. Addition of H_2SO_4–KCl; distillation at 145°C; derivatisation with $NaBEt_4$; GC separation followed by atomic fluorescence spectrometric detection.

Other techniques involved an ion-exchange procedure followed by AAS after UV irradiation, or a flow injection/microcolumn separation followed by cold vapour atomic fluorescence spectrometry. All these techniques were in good agreement in the certification of methyl-mercury in the two fish CRMs 463 and 464; they also gave satisfactory results in the two interlaboratory studies (intercomparison and certification) on methyl-mercury in sediment (in which other hyphenated techniques, e.g., involving HPLC, were successfully used).

4.3. Determination of organotin compounds

Tributyltin (TBT), used in antifouling paint formulations, is a source of major mortality of shellfish; triphenyltin is used as antifouling and herbicide agents and is also currently monitored. Two intercomparisons (solutions and TBT-spiked sediment) have been organised within the BCR-programme [27]. The project was continued by an interlaboratory study on TBT in a harbour sediment [28] which revealed the great analytical difficulties (which hampered certification) in the determination of TBT using hydride generation in this complicated

matrix, due both to the very low TBT levels (20 ng g^{-1} as TBT) and the presence of high amounts of inorganic and organic interferents. A study was carried out within the BCR to investigate these interferences [13].

The improvement achieved in the series of interlaboratory studies enabled a certification campaign to be organised and TBT and DBT could be certified in a coastal sediment (CRM 462) with levels of (70.5 ± 13.2) ng g^{-1} (as TBT) and (128 ± 16) ng g^{-1} (as DBT), respectively [29]. A separate project is being carried out under a BCR grant at the University of Plymouth to develop a HPLC–ID–ICP-MS method for the determination of butyltin compounds in environmental matrices [30].

The project on tin speciation is now focusing on the certification of butyl-and phenyl-tin in a mussel candidate CRM which was prepared in 1993. A feasibility study has shown that, whereas butyltins were stable at ambient temperature in the dark, the stability of phenyltins is more problematic [31], which implies that samples have to be stored at −20°C. The certification campaign will be conducted in the second half of 1996. The project will be continued by a certification campaign of organotins in a freshwater sediment.

In this project, the following hyphenated techniques using chromatography were successfully applied:

1. Acetic acid–hexane–diethyldithiocarbamate extraction; pentylation with Grignard reagent; capillary GC separation and detection by quartz furnace (T-tube) AAS.
2. Acetic acid extraction; hydride generation (with $NaBH_4$)-packed GC separation (cryogenic trapping) followed by quartz furnace (T-tube) AAS.
3. Diethylether–HCl–tropolone extraction–pentylation with Grignard reaction–capillary GC–MS.
4. Supercritical fluid extraction (CO_2–HCl–MeOH)–ethylation with Grignard reagent.
5. Capillary GC–FPD.
6. HBr–tropolone extraction–pentylation with Grignard reagent–capillary GC–FPD.
7. Acetic acid extraction–back-extraction with toluene–HPLC separation and ICP-MS detection.

All techniques summarised above were in good

agreement in the certification of TBT in the sediment CRM 462.

5. Conclusions

Hyphenated techniques using chromatography are now a major analytical tool for the determination of a wide variety of chemical species. The collaborative projects organised by the BCR-programme within the last decade have shown that most of the multi-step (hyphenated) techniques were in good agreement for the determination of e.g., TBT, methylmercury and trimethyllead in environmental matrices, providing that they are applied with drastic quality control precautions. The availability of certified reference materials will enable pursuit of the necessary optimisation and validation of these techniques. In particular, much remains to be done with regard to systematic studies for the evaluation of extraction recoveries, yields of derivatisation procedures, optimal chromatographic conditions and of course, on-line hyphenation of the different analytical steps.

References

[1] O.F.X. Donard and Ph. Quevauviller (Editors), Proceedings of the Workshop on Improvements of Speciation Analyses in Environmental Matrices, Mikrochim. Acta, 109 (1992) No. 1–4.

[2] Ph. Quevauviller and R. Morabito (Editors), Proceedings of the Workshop on Trends in Speciation Analysis - Discussion on organometallic speciation, Appl. Organomet. Chem., 8 (1994) No. 5.

[3] Ph. Quevauviller (Editor), Proceedings of the Workshop on Trends in Speciation Analysis - Discussions on inorganic speciation, Fresenius' Z. Anal. Chem., 351 (1995).

[4] E.A. Maier, Ph. Quevauviller and B. Griepink, Anal. Chim. Acta, 283 (1994) 590.

[5] O.F.X. Donard, in B. Welz (Editor), 5th Colloquium Atomspektrometrische Spurenanalytik, Perkin-Elmer, 1990, p. 395.

[6] M. Astruc, R. Pinel and A. Astruc, Mikrochim. Acta, 109 (1992) 73.

[7] R. Ritsema, Mikrochim. Acta, 109 (1992) 61.

[8] R. Rubio, A. Padró, J. Alberti and G. Rauret, Mikrochim. Acta, 109 (1992) 39.

[9] E.H. Larsen and S.H. Hansen, Mikrochim. Acta, 109 (1992) 47.

[10] I. Tolosa, J. Dachs and J.M. Bayona, Mikrochim. Acta, 109 (1992) 87.

[11] J.M. Bayona, J. Dachs, R. Alzaga and Ph. Quevauviller, Anal. Chim. Acta, 286 (1994) 319.

[12] A.G. Howard and S.D.W. Comber, Mikrochim. Acta, 109 (1992) 27.

[13] F.M. Martin, C.-M. Tseng, C. Belin, Ph. Quevauviller and O.F.X. Donard, Anal. Chim. Acta, 286 (1994) 343.

[14] W.M.R. Dirkx, R.J.A. van Cleuvenbergen and F.C. Adams, Mikrochim. Acta, 109 (1992) 79.

[15] E. Bailey and A.G.F. Brooks, Mikrochim. Acta, 109 (1992) 121.

[16] J.R. Ashby and P.J. Craig, Sci. Total Environ., 78 (1989) 219.

[17] O.F.X. Donard, Thesis No. 136, Univ. Bordeaux, France, 1987.

[18] R. Harrison and S. Rapsomanikis (Editors), Environmental analysis using chromatography interfaced with atomic spectroscopy, Ellis Horwood, Chichester, UK, 1988, p. 189.

[19] R.J.A. van Cleuvenbergen, W.M.R. Dirkx, Ph. Quevauviller and F.C. Adams, Int. J. Environ. Anal. Chem., 47 (1992) 21.

[20] Ph. Quevauviller, Y. Wang, A.B. Turnbull, W.M.R. Dirkx, R.M. Harrison and F.C. Adams, Appl. Organomet. Chem., 9 (1995) 89.

[21] Ph. Quevauviller, Y. Wang and R.M. Harrison, Appl. Organomet. Chem., 8 (1994) 703.

[22] A.A. Brown, L. Ebdon and S.J. Hill, Anal. Chim. Acta, 286 (1994) 391.

[23] Ph. Quevauviller, I. Drabaek, H. Muntau and B. Griepink, Appl. Organomet. Chem., 7 (1993) 413.

[24] Ph. Quevauviller, I. Drabaek, H. Muntau and B. Griepink, EUR Report, 15902 EN, European Commission, Brussels, 1994.

[25] Ph. Quevauviller, G.U. Fortunati, M. Filippelli, F. Baldi, M. Bianchi and H. Muntau, Appl. Organomet. Chem., in press.

[26] Ph. Quevauviller, G.U. Fortunati, M. Filippelli and H. Muntau, EUR Report, European Commission, Brussels, in press.

[27] Ph. Quevauviller, M. Astruc, L. Ebdon, H. Muntau, W. Cofino, R. Morabito and B. Griepink, Mikrochim. Acta, in press.

[28] Ph. Quevauviller, M. Astruc, L. Ebdon, G.N. Kramer and B. Griepink, Appl. Organomet. Chem., 8 (1994) 639.

[29] Ph. Quevauviller, M. Astruc, L. Ebdon, V. Desauziers, P.M. Sarradin, A. Astruc, G.N. Kramer and B. Griepink, Appl. Organomet. Chem., 8 (1994) 629.

[30] C. Rivas, L. Ebdon and S.J. Hill, Appl. Organomet. Chem., 8 (1994) 635.

[31] Ph. Quevauviller, S. Chiavarini, C. Cremisini, R. Morabito, M. Bianchi and H. Muntau, Mikrochim. Acta, 120 (1995) 281.