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Conclusions of the Workshop Trends in Speciation Analysis—An Overview of Discussions on Organometallic Speciation

Summary prepared by Ph. Quevauviller
European Commission, Measurements and Testing Programme, Rue de la Loi 200, B-1049 Brussels, Belgium

The development of analytical techniques for the determination of chemical species has been one of the growing features of the 1990s in analytical chemistry. The need for good quality control of these determinations has led the Measurements and Testing Programme (formerly the BCR) to organize series of interlaboratory studies in the field of speciation analysis over the last five years. The state-of-the-art speciation analysis has been discussed in a first workshop in 1990 (Arcachon, France) and, at this stage, it was thought necessary to discuss the progress achieved and the trends which should be developed in the near future. A workshop on Trends in Speciation Analysis was therefore held in Rome in February 1994 which allowed recommendations to be made based on round-table discussions. This paper gives a summary of these recommendations in the field of organometallic speciation. Projects currently undertaken in the field of organometallic speciation within the M&T programme are also described. An outline of the progamme and a list of the panel of experts participating in this workshop are given in the appendix.

INTRODUCTION

The determination of chemical species, known as speciation analysis, is nowadays performed routinely in many laboratories to control the quality of the environment, food and health. Some organometallic species are included in the list of substances mentioned in EC legislation: for example,

(a) the Council Decision 75/437/EEC (Marine Pollution from Land-Based Sources) mentions organic compounds of phosphorus, silicon and tin, and substances which may form such compounds in the marine environment, in the list of substances that require strict control (Annex II);
(b) these compounds are also considered in Annex II of the Council Decisions 77/585/EEC (Mediterranean Sea) and 77/586/EEC (Rhine River), specifying clearly that (for example) organotin and mercury compounds should be controlled;
(c) similar compounds are found in the Annex of the Council Directive 80/68/EEC (Groundwater).

Respect for this legislation and the need for a comparability of data produced worldwide require that the analyses are accurate. In order to improve and ensure a good quality control of speciation analysis, the Community Bureau of Reference, BCR (now the Measurements and Testing Programme), of the European Commission has organized a series of interlaboratory projects over the last five years as well as the production of certified reference materials (CRMs). The state-of-the-art of speciation analysis has been discussed in the framework of a BCR workshop held in Arcachon (France) in 1990.[1] Discussions allowed us to identify sources of error occurring at different steps and to propose solutions to solve them. At this stage it was thought necessary to discuss critical points usually not considered in classical interlaboratory studies, e.g. sampling and storage, as well as the progress achieved in the last four years, and the trends to be followed for further improving the quality control of speciation analysis. A second workshop on Trends in Speciation Analysis was therefore held in Rome on 20–22 February 1994; this paper gives a summary of the round-table discussion of this workshop. A brief overview of the projects on organometallic speciation currently carried out in the framework of the Measurements and Testing Programme is also given.

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THE MEASUREMENTS AND TESTING PROGRAMME—ROLE AND ACTION

The harmonization of measurement methodologies is a continuous process and may be achieved either by means of EC Directives or by the establishment of Norms (e.g. ISO or CEN standards). However, this does not solve all the problems. Indeed, the measurements and analyses required for the implementation of these Norms and Directives are sometimes so difficult that, even when aplying the same method, laboratories may still find very different results. It is obvious that such disagreement between laboratories does not allow regulations to be properly implemented and therefore these would have no harmonization effects. In order to eliminate disputes arising from doubtful measurements, the European Commission established the Community Bureau of Reference (BCR) about 20 years ago to encourage and support technical collaboration between the 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 as a whole: trade, agriculture, food, industrial products, environment, health and consumer protection. To pursue this action, the European Commission has implemented the Measurements and Testing Programme which, by addressing the issues highlighted above, aims to contribute to the harmonization and improvement of methods of measurement and analysis when these methods are not sufficiently accurate and laboratories obtain different results. In practice, whereas the action of the BCR was limited to the organization of interlaboratory studies and production of certified reference materials (CRMs), the Measurements and Testing 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 at present supporting the development of new methods of measurements ands pre-normative research (in support of activities of normative bodies, e.g. CEN).

One of the major tasks of the Measurements and Testing Programme essentially consists of organizing projects in which participating laboratories may collaborate to improve the measurement or analysis concerned. The implementation of projects usually follows a stepwise approach in at least two major phases, described below.

Step-by-step approach

The analytical methods used for the determination of chemical forms of elements are based on successive steps which may vary from one procedure to another. Methods have their own particular source of error. For instance, for some techniques, errors may occur due to an incomplete derivatization, a step which is not necessary for other techniques such as high-performance liquid chromatography (HPLC); HPLC, 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 derivatization/gas chromatography (GC)/atomic absorption spectrometry (AAS) and HPLC/Inductively Coupled Plasma Mass Spectrometry (ICP MSD). If the methods have similarities, such as an extraction step, a comparison of the results will most probably lead to conclusions concerning the accuracy of the method of final determination, and not the analytical result as a whole. Interlaboratory studies are therefore valuable tools to evaluate analytical techniques;[2] in particular, a good procedure to evaluate the performance of multi-step techniques is to examine separately the different steps and evaluate the sources of error which may arise. To do so, different samples, previously characterized for their homogeneity and stability, are prepared and sent to the participating laboratories. Typical matrices are:

(1) solutions containing one of 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 fully the performance of the separation on real samples;
(3) raw extracts, to verify the clean-up procedure;

(4) real matrices homogeneously enriched and equilibrated with the analyte(s) to be determined, to test the total analytical procedure;
(5) real samples.

This evaluation enables the sources of error to be identified at each analytical step and consequently help the laboratories to remove them. Some of the errors likely to occur in speciation analyses are discussed elsewhere.[1]

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 a destruction of the sample by dissolutions, calcinations 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 possibility for any laboratory to ensure traceability in a simple manner is to verify the analytical procedure by means of a so-called matrix RM (reference material) 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 values is thus warned that its measurement includes error(s) of which the source must be identified. Thus, CRMs having well-known properties should be used to:

(a) verify the accuracy of results obtained in a laboratory;
(b) monitor the performance of the method (e.g. cusum control charts);
(c) calibrate equipment which requires a calibrant similar to the matrix (e.g. optical emission spectrometry, X-ray fluorescence spectrometry);
(d) demonstrate equivalence between methods;
(e) detect errors in the application of standardized 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 realize that, owing to discrepancies in composition between CRMs and unknowns, 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 a good quality assurance (QA). The CRMs produced are as close as possible to real matrices, to match the analytical difficulties encountered in the analyses of environment samples. Beside its role of method performance evaluation, a CRM as prepared by the BCR can also 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.[3]

CURRENT PROJECTS ON ORGANOMETALLIC SPECIATION

This section gives an account of projects on organometallic speciation currently being carried out within the Measurements and Testing Programme.

Determination of trimethyl- and triethyl-lead compounds

Although the consumption of lead-containing gasoline should decrease in the future, the ubiquity of organolead compounds (mostly methyl- and ethyl-lead species) in the environment appears to be likely to continue for some time. Due to the presently high contamination levels in the environment, it is expected that the determination of these compounds will be carried out for the next 10–20 years for continuous monitoring of atmospheric contamination. The BCR has consequently started a project aiming to organize an intercomparison on solutions of pure trimethyl-lead species. The stability of this species in solution has been investigated[4] and a first exercise on trimethyl-lead in solutions was successfully concluded in 1993.[5] A further development has focused on the preparation of artificial rainwater and urban dust for a second interlaboratory study on trimethyl-lead, the results of which, and expected developments, are presented in this issue.[6] The preparation of candidate reference

materials of artificial rainwater and urban dust is currently in progress for a certification to be possibly organized in 1995; this project is coordinated by the University of Birmingham (Professor R. M. Harrison). A separate project was carried out within the BCR to develop an HPLC–ID–ICP MS method for lead speciation which could be used in the certification;[7] this project is coordinated by the University of Plymouth (Dr S. Hill).

Determination of methylmercury

Methylmercury (MeHg) is known to accumulate in the food chain and to lead to 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 intercomparisons of solutions of pure analytes and fish extracts.[8] 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 run a third intercomparison with other fish extracts to remove the remaining biases, 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 organization of a certification campaign of two tuna-fish materials (with low and high levels of MeHg) which was conducted in 1992/93. The CRMs 463 and 464 are presently available;[9] these materials contain 3.04 $\mu g\,g^{-1}$ and 5.50 $\mu g\,g^{-1}$ methylmercury, respectively. The project was managed by the Danish Technological Institute (Dr I. Drabaek).

The efforts to improve the quality control of MeHg determination in the environment are now continuing in the framework of an M&T project which is coordinated by the Studio di Ingegneria Ambientale in Milan (Dr U. Fortunati); the project aims to certify the contents of MeHg in a freshwater or lagoon sediment.

Determination of butyl- and phenyl-tin compounds

Tributyltin (TBT), used in antifouling paint formulations, is a source of major mortality of shellfish. The use of TBT-containing antifouling paints is regulated and organotin compounds are now included in EC Directives as substances to be controlled in the environment (see the Introduction). Two intercomparisons (solutions and TBT-spiked sediment) have been organized within the BCR programme.[10,11] The project was continued by an interlaboratory study on TBT in a harbour sediment[12] which revealed the analytical difficulties 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 to 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 organized and TBT and DBT in a coastal sediment could be certified (CRM 462) with levels of $(70.5 \pm 13.2)\ ng\,g^{-1}$ (as TBT) and $(128 \pm 16)\ ng\,g^{-1}$ (as DBT), respectively. The results of this certification are described in detail in this issue.[14] The project was coordinated by the University of Pau (Professor M. Astruc) and the University of Plymouth (Professor L. Ebdon). A separate project is carried out under a BCR grant at the University of Plymouth (Miss C. Rivas) to develop an HPLC/ID–ICP MS method for the determination of butyltin compounds in environmental matrices.[15]

The continuation of the project on tin speciation is focusing on the preparation of freeze-dried mussel samples to be certified for their contents of butyl- and phenyl-tin compounds. A feasibility study has shown that, whereas butyltins are stable at ambient temperature in the dark, the stability of phenyltins is more problematic.[16] Further investigations are currently being carried out to establish the optimal storage conditions of this candidate CRM; this project is coordinated by ENEA in Rome (Dr R. Morabito).

SUMMARY OF THE ROUND-TABLE DISCUSSIONS

The following section summarizes the minutes of the round-table discussions as reported by the chairpersons and rapporteurs at the workshop on Trends in Speciation analysis (see annexes 1 and 2).

Sampling and storage

When establishing a sampling programme, consideration should be given to the following four areas:

(*a*) *Objectives*. The objectives of the proposed programme should be carefully defined. Examples here include sampling for purposes of determining spatial distribution of contaminants in environmental samples or trends with time, or sampling for health assurance purposes. At this stage the requirement for speciation should be considered. Some species are operationally defined, e.g. reactive mercury, and some may be matrix-specific. It is important to involve the data users in all planning.

(*b*) *Matrix identification*. Discussion here was restricted to consideration of water, sediment and some types of biota. Since species may be matrix-specific, the most appropriate sample should be collected. Examples here include redox control of species in sediments, metabolic control of compounds in biota and distribution of species within dissolved and particulate phases in water, or porewater.

(*c*) *Sampling strategy*. All aspects of sampling variability should be considered. Species within some matrices such as water may be subject to short- and long-term temporal changes, and spatial heterogeneity with depth and distance from point sources of contaminants. The heterogeneity of the matrix should be investigated before major sampling programmes are undertaken. Both inter- and intra-sample (e.g. within mussel tissues and between individuals) variability should be established. The sampling event should not be considered in isolation from the rest of the analytical programme, and the requirements for clear sampling technique should be appropriately designed for the detection limits of the analysis. Losses due to volatilization or surface adsorption should be considered, in addition to contamination risks. In addition, the stability of the species should be investigated and examined during storage and shipment. Finally, continuous (time-integrated) rather than discontinuous sampling may be a useful approach in reducing variability. A sound statistical basis for sampling should be established.

(*d*) *Validation and documentation*. The validity of sampling techniques is generally established by consensus opinion. Where recommended techniques exist they should be adopted, and there is a case here for providing 'Certified Recommended Sampling Strategies' based on results from experienced laboratories. Whatever sampling strategy is adopted, it should be well documented by standard operating procedures, and samplers should be tested, e.g. in the framework of interlaboratory studies. Written protocols in areas such as statistical design, sampling methods, storage and preparation as well as analytical methods were thought necessary.

Many participants agreed that the collection of composite samples is an appropriate approach. However, it is important to test variability in individual samples occasionally. More heterogeneous samples require larger sample size, but it is difficult to determine how large. In this respect, sediment samples are probably more difficult to collect than aqueous or biological samples.

With regard to sample conservation, the containers used most often are made of acid-treated glass, polycarbonate, and Teflon. There was a general agreement that water samples should be filtered, acidified, and stored at 4 °C. Biological samples may be stored frozen; some workers freeze-dry samples before storage. For sediment analysis, nearly every worker has studies showing that various storage techniques result in loss of various analytes. Storage at 4 °C or by freezing is used, but certain analytes decompose under these conditions. Freeze-drying is another approach, but volatile analytes could be lost during this procedure. Systematic studies on effects of storage on the stability of chemical species were recommended to be carried out.

Extraction

Extraction of organometal analytes from samples is a complicated matter in which two conflicting issues need to be combined: obtaining an adequate recovery on one hand, and preventing losses, especially destruction of the analyte, on the other. The participants could not see at present much advance in this issue in comparison with the results of the Arcachon discussion.[1] It was stressed that safe methods for extraction would need to be specifically designed for each individual analyte in a specific matrix; in this view, a common strategy could be followed in which specific conditions would be adopted (reagent, time, heating, sonification) and tested on samples supplied for intercomparison/certification. The samples studied should be natural samples. Protocols should be established to describe (1) the extraction procedure of a test extractant solution without the solid sample to be analysed (to

test the analytical procedure), (2) the analysis and (3) the re-extraction of the sample after the determination (which is necessary, at least once).

A Standard Addition must be applied to test the recovery, but a number of participants doubted that the recovery of the spike always corresponds with that of the analyte from the sample; there was argument on the use of spiking solutions, although for sediments it was generally agreed that spiked compounds should be added in aqueous solution, if necessary previously wetting the material and allowing a sufficient time to reach equilibration (24 h has been proposed). Freeze-dried materials should be dried again before analysis.

Spiking experiments were thought to be particularly important, although not without their problems. It was generally agreed that there should be a protocol for spiking procedures. Problems with spiking experiments include the fact that they are not applicable to all types of sample, e.g. biological cells; they may be sample-dependent and often need to be supported by kinetic studies. In many cases, there is also the need to establish whether we wish to look at absolute recovery or analytical error. It was concluded that although our present knowledge is not perfect, the use of spiking experiments helps to minimize errors. It was also thought that the technique could be enhanced if used in conjunction with radiolabelled materials; there was, however, no unanimity on the utility of isotopic or radioactive experiments for the assessment of recovery unless the isotopic exchange or the radioactive tracer is part of the analyte in the sample.

A general agreement appeared on the convenience of checking extraction efficiency, at least in a duplicate extraction experiment, over the same sample. Although there is a temptation to use aggressive methods to ensure total extraction, violent methods may degrade the sample. This discussion moved on to look at other possible approaches. Individual members discussed the importance of water content for accurate determinations from biological materials. For this matrix the utility of enzymatic hydrolysis for the determination of butyltins was emphasized, although there is evidence of decomposition of triphenyltin to monophenyltin in such a treatment.

It was generally agreed that new techniques should be developed in the future. The promising development of supercritical extraction (SFE) techniques and microwave methods was highlighted. In the former case, SFE may be used to replace hexane and toluene commonly used in conventional extraction methods, although the problems due to the extra complexity and expense were noted. In the latter case, if microwave methods are to be used effectively, the transmission of energy to the matrix needs to be investigated. Microwave techniques lend themselves to on-line approaches and the use of flow injection methodologies. Ultrasonic extraction was also recommended; most of the participants agreed that, at any moment, this could be the procedure of choice.

Finally, the need for new reference materials was identified; examples were multi-arsenic species reference materials ideally incorporating radiolabelled material in the matrix to maximize their utility for biological studies; simple reference materials of known matrix (ideally a sediment) with an intermediate concentration of analyte (i.e. not so low that it strains the analytical capabilities of the technique, but not so high that it becomes totally unrepresentative or requires excessive dilution for most techniques).

In general the group assumed that the contradictory requirements of full extraction and of preservation of the identity of analytes are difficult to combine for the time-being. The importance of further coordinated efforts on the issue was stressed.

No significant advances have been made from the Arcachon meeting until now. Very similar questions were on the table and so far have not been fully answered. Quality control of extraction processes continues to be difficult and it is not clear how to separate the different uncertainties associated to the process.

Derivatization

Perhaps the most important point raised in the discussions was that derivatization should be avoided if at all possible, both to simplify the analytical methodology and to avoid one potential source of contamination, analyte loss and artifact formation. For improved introduction of the analyte into the detector system, some form of post-column derivatizations may nevertheless be required. In this case, some of the aforementioned problems will be reduced, as following separation on the column, the analyte species are more or less isolated from the matrix. One such example was given, involving the post-column photolysis of arsenic species followed by hydride

generation after liquid-chromatographic separation. In this way, arsenobetaine and arsenocholine became amenable to hydride generation after conversion to As(V).

The other main concern of the group in terms of derivatization was that all information about the counter-ion(s) is lost. The relevance of derivatization methods was discussed in the perspective that ligands (biological and abiological) most often determine the environmental fate and toxicokinetics of metallic species. The biological coordination chemistry of inorganic and organic arsenic, mercury and tin species was briefly discussed to illustrate this somewhat neglected aspect of speciation. On the other hand, it was mentioned that in the aquatic environment the relative toxicities of various tin species does not appear to relate to counter-ions; this aspect should be studied along with the relationships with humic, fulvic and peptide ligands. On this point, the group felt that it was an inherently limiting aspect of derivatization that part of the original analyte molecule is lost. This raised the question of exploring liquid-chromatographic–spectroscopic methods in order to obtain more information about biological and abiological ligands interacting with metallic species.

The remainder of the discussion then focused on pre-column derivatization techniques prior to gas chromatographic separation, and highlighted several major problem areas:

(1) derivatization 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 derivatization (such as extraction, pre-concentration 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.

Concerning the derivatization methods employed by the group members, the following observations, comments and recommendations were made:

(*a*) *Hydride generation*. Difficulties in recovering added species (e.g. tributyltin and triphenyltin) as hydrides were noted, as well as large variabilities between different matrices. In some cases, this may be due to interferences from transition-metal ions in the sample solution or digest, which can be minimized using a masking agent such as L-cysteine. Otherwise, the tributyltin cation may be associated with lipophilic material and thus not available for the hydrization reaction which occurs in the aqueous phase when using sodium tetrahydroborate ($NaBH_4$). This problem may be overcome using 'phase transfer catalysis' where the tetrabutylammonium salt of the tetrahydroborate ($Bu_4N^+ BH_4$) is used instead, as this will even hydridize species present in lipophilic phases.

The group noted recent work on the speciation of mercury(II) and methylmercury using hydride generation. It was generally believed that hydride generation would not be a practicable method for organolead analysis in real samples.

(*b*) *Aqueous phase ethylation*. This technique is clearly growing in popularity because extraction into an organic phase is avoided and one source of analytical uncertainty is therefore eliminated. Artifact formation and problems with impurities relating to the use of Grignard reagents are also greatly reduced. However, for the determination of methylmercury, problems have been observed due to the conversion of inorganic mercury to the ethyl-methylmercury derivative in the presence of the ethylation reagent. Batch-to-batch variations in the quality of the commercial reagent and spurious peaks in the chromatograms also indicated that caution should still be exercised in the use of $NaBEt_4$.

Large amounts of the reagent may be consumed by the sample matrix, particularly by natural waters rich in humic substances and sea salts, and sulfidic sediments, leading to incomplete ethylation of methylmercury. Thus extraction techniques are often required, and generally the sample pre-treatment steps must be carefully optimized for every sample type.

(*c*) *Grignard alkylation followed by GC–MIP–AES* (Gas Chromatography–Microwave Induced Plasma–Atomic Emission Spectrometry). With the increasing use of this sequence, the subpicogram detection limits obtained for lead, tin and mercury species has necessitated a re-evaluation of blank levels originating from Grignard reagents. Ultra-trace analyte impurities and low-level contamination from other alkylmagnesium halides may lead to detectable quantities of undesirable species in the chromatograms. There may be considerable differences in reagent quality and

purity between different commercial sources, between alkylating reagents and on a batch-to-batch basis. Following derivatization, destruction of the excess reagent may result in decomposition of certain products, e.g. phenyltin derivatives.

Problems of unidentified artifactual GC peaks and purity of commercially available Grignard reagents raised some concerns.

General conclusions were:

(1) Better contrast of the purity of derivatization reagents should be exercised. As manufacturers are unlikely to do this, the responsibility for reagent testing will probably depend on the analytical laboratory.
(2) There is a definite need for calibrants to be used in assessing the efficiency of analyte derivatization.

Kinetic aspects were discussed in terms of both matrix effects and analyte concentration. Microwave-assisted derivatization was suggested to be an efficient approach to increase efficiency.

Separation

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.

The group concluded that the problems experienced with capillary column gas chromatography were generally the same as those encountered in trace organic analysis. An exception was methylmercury analysis, which requires column conditioning with mercury chloride, for example, to maintain column performance. As already stressed at the Arcachon workshop,[1] mercury chloride conditioning was not recommended because of the risk of possible artifact formation. However, quality control of the column condition was recommended. It was agreed that injection volume limitations have been partially overcome by the use of retention gaps or solvent venting techniques. Programmable temperature injectors were recommended for use with less volatile analytes, to prevent analyte loss during venting.

Packed column gas chromatography, although robust and relatively inexpensive, suffers from lower resolution and is not compatible with atomic emission or mass selective detection. The use of packed columns as a trapping technique for hydride or ethylates was, however, found useful. Although, the use of packed column gas chromatography results in lower detection limits, the coupling to a highly sensitive detector such as an atomic fluorescence spectrometer will still provide a good analytical system.

The group noted that suitable internal standards remain difficult to select, requiring a suitable retention time and a similar chemical structure to that of the analytes to be determined. It was recommended that internal standards with an altered isotopic ratio be used if adequate instrumentation was available.

There also appeared to be broad agreement that more thought and effort should be spent on the chromatographic side of linked liquid chromatography–detector systems. The general view was that this area had not attracted the attention that it required or that had been applied to other aspects of separations. Members of the group reported their experiences with the non-reproducibility of columns which were however stated by manufacturers to be identical. More information about the preparation and details of columns were required from the suppliers; possibly some collaboration with suppliers/manufacturers would be beneficial. The 'inertness' of columns was questioned. It appeared in the discussions that columns were not as inert as manufacturers had indicated.

There was much support for hyphenated systems using mass spectrometry for detection, e.g. LC–MS and CZE–MS systems (CZE = capillary zone electrophoresis). Electrospray and ion-spray mass spectrometry were believed to have considerable potential. The use of ICPMS at low potential to reduce fragmentations (even to provide molecular species) was advocated; this would clearly provide more structural information. The possibilities of adding unseparated mixtures directly into the mass spectrometer (e.g. using electrospray MS and MS–MS set-ups) were raised. With the continuing development of NMR spectrometry, hope was expressed that this technique may become an important tool in the not-too-distant future. Electron spin resonance (ESR/EPR) was also mentioned as being worthy of study as a means to speciation.

Contact with analysts working in organic chemistry and in life sciences was generally considered to be advantageous. There is a great accumulation of data/techniques in these areas of

analysis which could provide new ideas and possibilities for speciation analysts.

CONCLUSIONS

The workshop on Trends in Speciation Analysis enabled us to consider analytical problems in the determination of organometallic species through round-table discussions ranging over various different topics (sampling, storage, extraction, derivatization and separation). The trends in organometallic speciation were examined in a plenary round-table and the following needs were identified.

—Fundamental research on the occurrence and fate of new species (toxicity, environmental pathways) and development of new analytical techniques for their determination; examples were larger molecule species, e.g. metalloproteins and metalloenzymes, and organoselenium compounds.
—Development of new techniques, e.g. sensitive detection techniques coupled to electrophoresis (e.g. protein-bound nickel species); tools to select ions to avoid interferences in ICP MS detection (ion trap); chromatographic tools adapted to speciation; coupling capillary electrophoresis, HPLC or GC to fluorescence spectrometry to be used for field measurements (e.g. for Hg, Se, Cd, Pb species); fiber optics/field-based techniques; miniaturized microwave focused systems to be used in-line with detection; and so on.
—Preparation of isotopically labelled compounds as they are present in matrices, e.g. ^{82}Se-labelled methionine in food, which can possibly be produced by biosynthesis, e.g. ^{82}Se-labelled cysteine given to yeast.

Finally, it is necessary to establish links between speciation experts and organic chemists and biochemists.

The conclusions of the round-table discussions on *inorganic* speciation have been summarized in the same format as this paper and are presented in a special issue of *Fresenius' Journal of Analytical Chemistry* (vol. 350, 1994) together with all the participants' contributions dealing with general aspects of speciation analysis and inorganic speciation. The present issue includes all the contributions dealing with tin, mercury and lead speciation.

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15. S. J. Hill, A. Brown, C. Rivas, S. Sparkes and L. Ebdon, in: Quality Assurance for Environmental Analysis, Ph. Quevauviller, E. A. Maier and B. Griepink (Eds), Elsevier, Amsterdam, 412 (1994).
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APPENDIX 1

The laboratories invited were selected on the basis of their active participation in BCR projects on speciation analysis and their recognized know-

ledge in this field. The following list indicates the experts who participated in the round-table discussions on organometallic speciation.

Round-table on organometallic speciation—Group 1

F. Adams	University of Antwerp (B)
M. Astruc	University of Pau (F)
D. Baxter	University of Umeå (S)
A. Bortoli	Presidio Multizonale di Prevenzione, Venice (I)
R. Cela	University of Santiago de Compostela (E)
C. Cremisini	University 'La Sapienza', Rome (I)
W. Dirkx	Betz Europe Laboratory, Heverlee (B)
L. Ebdon	University of Plymouth (UK)
M. Filippelli	Presidio Multizonale di Prevenzione, La Spezia (I)
D. Forsyth	Health and Welfare Canada, Ottawa (CND)
Å. Iverfeldt	Swedish Environmental Research Institute, Göteborg (S)
B. Lalère	University of Bordeaux (F)
F. Martin	University of Bordeaux (F)
V. Minganti	University of Genoa (I)
R. Morabito	ENEA, Rome (I)
C. Nerin	University of Zaragoza (E)
G. Rauret	University of Barcelona (E)
R. Ritsema	RIVM, Bilthoven (NL)
C. Rivas	University of Plymouth (UK)
J. H. Weber	University of New Hampshire (USA)

Round-table on organometallic speciation—Group 2

A. W. Benbow	Fresenius Institute, Taunusstein (D)
J. Bettmer	University of Münster (D)
J. S. Blais	McGill University, Québec (CND)
S. Chiavarini	ENEA, Rome (I)
P. Colombini	University of Pisa (I)
P. J. Craig	De Montfort University, Leicester (UK)
O. F. X. Donard	University of Bordeaux (F)
U. Fortunati	Studio di Ingegneria Ambientale, Milano (I)
J. L. Gomez-Ariza	University of Sevilla (E)
U. Harms	Bundesforschungsanstalt für Fischerei, Hamburg (D)
S. Hill	University of Plymouth (UK)
E. H. Larsen	National Food Agency, Søborg (DK)
R. Lobinski	University of Antwerp (B)
O. Nygren	National Institute of Occupational Health, Umea (S)
J. L. Rocca	University of Lyon (F)
R. Rubio	University of Barcelona (E)
M. Siu	National Research Council Canada, Ottawa (CND)
J. Stäb	NV Duinwaterbedrijf Zuid-Holland, Voorburg (NL)
M. Waldock	MAFF, Burnham-on-Crouch (UK)
J. Wardell	University of Aberdeen (UK)
C. Witte	University of Antwerp (B)

Key: B, Belgium; CND, Canada; D. Germany; E, Spain; F, France; I, Italy; NL, The Netherlands; S, Sweden; UK, United Kingdom; USA, United States of America.

APPENDIX 2

The workshop consisted of a series of plenary lectures and round-table discussions on different topics. Each round-table was chaired by one expert and the minutes were taken by a rapporteur. Each group had to discuss each of the four topics independently:

A: Sampling and storage.
B: Extraction.
C Derivatization.
D Separation.

In addition, a plenary round-table discussed the trends expected in the development of hyphenated techniques. The task of each chairman was to give a short introduction of the topic of the round-table and to lead the discussions. The rapporteurs took minutes of the discussions which were summarized at the end of the session. The chairman and rapporteurs of each round-table are listed in the agenda below.

Programme

20 February 1994
Opening of the workshop
Plenary lecture on Sampling and storage

(Topic A): L. Ebdon
Round-table Group 1: chaired by R. Morabito; rapporteur, J. H. Weber
Round-table Group 2: chaired by O. F. X. Donard; rapporteur, M. Waldock

Plenary lecture on Extraction (Topic B): R. Morabito
Round-table Group 1: chaired by F. Adams; rapporteur, R. Cela
Round-table Group 2: chaired by R. Lobinski; rapporteur, S. Hill

21 February 1994
Plenary lecture on Derivatization (Topic C): F. Adams
Round-table Group 1: chaired by M. Astruc; rapporteur, D. Baxter
Round-table Group 2: chaired by J. S. Blais; rapporteur, P. J. Craig

Plenary lecture on Separation (Topic D): R. Lobinski
Round-table Group 1: chaired by D. Forsyth; raporteur, G. Rauret
Round-table Group 2: chaired by E. Larsen; rapporteur, J. Wardell

22 February 1994
Plenary lecture on Trends in hyphenated techniques: E. Larsen and O. F. X. Donard