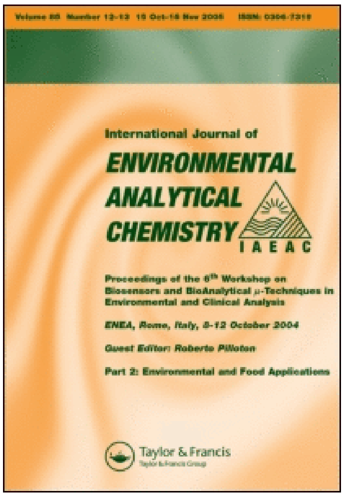

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The EC-SM & C Programme in Support to the Improvement of Quality Control of Environmental Analysis

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THE EC-SM&T PROGRAMME IN SUPPORT TO THE IMPROVEMENT OF QUALITY CONTROL OF ENVIRONMENTAL ANALYSIS*

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The Standards, Measurements and Testing Programme (SM&T) of the European Commission (continuation of the BCR and Measurements and Testing Programmes) aims to contribute to the harmonization and improvement of methods and measurements carried out within the European Union and hence to the comparability of data necessary for e.g. trade activities, monitoring of environment, food and health, etc. One of the tool currently used to achieve this goal is the organization of interlaboratory studies (intercomparisons and certifications of reference materials) in which laboratories may collaborate to improve the measurement or analysis concerned. Other activities are related to development of new methods and prenormative research. Examples of projects undertaken within the Measurements and Testing Programme (1990-94) are given in this paper, covering different aspects, namely interlaboratory study on modern pesticides in freeze dried water, certification of Cr-species in water and welding dust, evaluation of extraction and derivatization procedures in organotin speciation analysis, network on harmonization of leading/extraction tests for environmental risk assessment, and proficiency testing scheme applied to marine monitoring (QUASIMEME project).

Keywords: Quality control; modern pesticides; chromium speciation; tin speciation; leaching/extraction tests; marine monitoring

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[*] This paper summarises six oral communications which were presented in the frame of a special session within the 26th International Symposium on Environmental Analytical Chemistry held in Vienna on 9-12 April 1996.

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OBJECTIVES OF THE SM&T PROGRAMME

The lack of quality control of analyses performed in routine, industrial and research laboratories may create strong economic losses due to the possible misuse of inaccurate data (e.g. in modelling applications, decisions on the management of the quality of environment, food and health, trade activities) and consequent burdens (e.g. action courts, doubts of the public on government decisions). Quality has thus become one of the priority items of the 90's and a wide variety of actions has been undertaken in many countries to verify the quality of data produced; these actions included the implementation of accreditation systems, QA guidelines and norms (e.g. ISO 9000 and EN 45000 series), organization of interlaboratory studies, proficiency testing and production of laboratory and certified reference materials. In Europe, The Community Bureau of Reference (BCR) of the European Commission has been active within the last 25 years in the field of quality assurance of measurements. This action has been pursued by the Measurements and Testing Programme, M&T (Third Framework Programme: 1990-94) and the current programme, renamed Standards, Measurements and Testing Programme, SM&T (Fourth Framework Programme: 1994-98)[1]. The objective of this Research and Technology Development (RTD) programme is to improve the quality of measurements and consequently harmonize the results obtained within the European Union particularly in support to EC regulations (compliance with EC Directives), standardization (e.g. pre-normative research) and means of calibration (transfer standards in metrology, CRMs in chemistry). Emphasis is given, in the current programme, to the support to Measurements for Quality European Products and Written Standards for Industry (Theme I), Research related to Written Standards and Technical Support to Trade (Theme II) and Measurements related to the Needs of Society (Theme III).

PARTICIPATION IN THE SM&T PROGRAMME

Equally to other RTD programme of the DG XII of the European Commission, the participation in the SM&T programme is open to all legal entities. RTD projects may be submitted in the frame of time-limited calls for proposals. A first call has been opened on Theme I in 1994[1]; a second call was concluded in 1995 on Themes II and III, of which the projects will be listed elsewhere[2]; further calls were organised in 1996 (Theme I) and 1997 (Themes II and III). In parallel to these calls, dedicated calls in support of Community policies were organised at regular intervals in response to requests from other General Directorates or normalising bodies, e.g. to establish a technical basis for the implementation of directives or standards.

The SM&T programme also offers the possibility to propose thematic networks on various topics with the aim to create links between research organizations and industry. Finally, accompanying measures may be proposed, e.g. organization of scientific workshops or training actions, submission of doctoral or post-doctoral grants (in support to projects selected for funding) etc.

EXAMPLES OF PROJECTS IN THE FIELD OF ENVIRONMENTAL ANALYSIS

The projects currently selected in the frame of SM&T calls for proposals deal with four main types of activities, namely (i) interlaboratory studies, (ii) certification of reference materials, (iii) pre-normative research and (iv) development of new methods or instrumentation. The projects described below are currently funded by the SM&T programme.

Interlaboratory Study on Modern Pesticides in Freeze Dried Water[3]

One of the best ways to assess the performance of analytical methods is to compare them in the frame of interlaboratory studies[4]. The comparison of different techniques as applied in different laboratories allows to detect sources of error due to a particular method, or part of a method (e.g. insufficient extraction, uncontrolled interferences), or to a lack of quality control within one laboratory. The participation in such interlaboratory studies may then help in establishing the state of the art of a particular field of analysis and to improve the quality of the measurements. These studies are often carried out to remove all sources of error in the application of techniques to be used in certification campaigns or to test the performance of a standardized method prior to its adoption as an official standard.

An example of interlaboratory study organized prior to certification is illustrated by the project on modern pesticides in freeze dried water: this project aiming to certify modern pesticides in freeze dried water started some years ago by a feasibility study on sample preparation[5]. A series of polar pesticides (atrazine, simazine, fenitrothion, fenamiphos, parathion-ethyl, carbaryl, permethrin, propanil and limuron) at low concentrations (from 0.02 to 90 $\mu g.L^{-1}$) were dissolved in tap water containing 10 $g.L^{-1}$ of glycine. The complete reconstitution of this material was rather difficult and time consuming due to the presence of glycine added as a stabilizer during lyophilisation; in addition, glycine created some analytical difficulties owing to matrix effects which hampered the certification of the first batch of candidate reference material (lyophilised solution). In view of solving these difficulties, the project has continued in the frame of the M&T programme by the preparation of a spiked aqueous solution containing 2.5 $g.L^{-1}$ of NaCI used to stabilize selected pesticides (atrazine, simazine, carbaryl, propanil, linuron, fenamiphos and permethrin) during lyophilisation; this sample was used in an interlaboratory study involving 20 participants which aimed to improve the state of the art of polar pesticide determinations in water prior to the certification of a candidate CRM. The preparation, the homogeneity and stability of lyophilised water samples containing the above mentioned pesticides were studied; the final concentration of each pesticide in water was in the range 50-80 $\mu g.L^{-1}$. After lyophilisation, the residue was rehomogenised and bottled in amber glass bottles and stored at -20°C and +20°C; the stability was monitored over a period of three months. Pesticide determinations were carried out by high performance liquid chromatography with diode-array detection except permethrin which was determined by gas chromatography with electron capture detection.

The results obtained showed that the samples were homogeneous with regard to atrazine, carbaryl, propanil, linuron and fenamiphos contents, whereas simazine and permethrin were not homogeneously distributed. With respect to stability over three months, all the pesticides were found to be stable at -20°C; at +20°C, atrazine, simazine, carbaryl, propanil and linuron were stable over the duration of the study whereas a decrease of ca. 70% in fenamiphos content was observed. The results of the interlaboratory study (comparing different analytical methods used by different participants) were in satisfactory agreement for most of the determined pesticides. However, discrepancies were still observed for permethrin, likely due to the low concentrations in the samples and the lack of homogeneity of this compound. With this exception, it could be concluded that the freeze-drying procedure tested and the performance of the analytical techniques tested were suitable for the organisation of a possible certification of most of the polar pesticides considered in this study. The next step of this project has focused on the preparation of 6000 litres of water enriched with the above mentioned pesticides and lyophilised; the verification of the homogeneity and stability of this candidate CRM is currently being studied.

Certification of Cr-Species[6]

The use of CRMs to control the quality of chemical analysis is now widely recognised[3]. These materials are prepared in such a way that they match the composition of real samples and hence may be used to verify the performance of methods within the laboratory at regular intervals, without being obliged to participate in time-consuming interlaboratory studies[3]. The production of such materials within the Measurements and Testing Programme usually follow interlaboratory studies in which expert laboratories, having proved the quality of their analysis, are selected.

A certification campaign recently concluded (Cr-species in lyophilized solutions and welding dust) illustrates this item: the different toxicity and bioavailability of Cr(III) and Cr(VI) are a public health concern and, therefore, require strict control. Cr(III) is found to be essential for man, whereas the deleterious effects to living organisms of Cr(VI) are well documented. Cr(VI) is a potent carcinogenic agent for the respiratory tract, requiring continuous monitoring of occupational air. Hence monitoring of the separate species in e.g. drinking water, river water, occupational exposure or environmental samples is necessary since the determination of total chromium does not provide sufficient information about possible health effects.

The SM&T project on Cr-speciation has been initiated in 1988 by a doctoral grant of which the aim was to investigate the feasibility of preparing candidate reference materials[7]. Some years later, interlaboratory studies on Cr(III) and Cr(VI) in freeze dried water and filters loaded with welding dust were successfully concluded[8]. The candidate reference materials were prepared in such a way that their composition matched the one of natural samples with concentrations similar to those stipulated in the EC directives. Two types of reference materials were prepared with certified Cr-species:

CRM 544: a lyophilized solution with Cr(III) and Cr(VI) contents as found in natural or tap water and a total Cr content less than 50 µg/L (following the EC Directive 80/778/EEC, L229/20, D48 on the quality of drinking water); CRM 545: filters loaded with welding dust, containing approximately 100 µg Cr(VI) per mg dust which is the level normally encountered on the personal filter monitors of stainless steel welders. Directive 90/3941/EEC imposes a continuous monitoring on carcinogenic substances, including Cr(VI). In occupational health, the Occupational Exposure Limit (OEL) for water soluble and certain water insoluble compounds in indoor air is limited to 0.5 $mg.m^3$ for Cr(III) and to 0.05 $mg.m^3$ for Cr(VI).

Both products are homogeneous and contain stable Cr(III)/Cr(VI) species. These candidate CRMs have been analyzed by a group of expert laboratories and the results were thoroughly discussed in a technical meeting. The results of this certification has been compiled in a report[9]; the materials are available at the Institute for Reference Materials and Measurements (Geel, Belgium).

Evaluation of Analytical Steps Prior to Certification of Tin Species[10]

One of the task of the SM&T programme is to support the development of new instrumentation, either novel techniques for the determination of environmental parameters within the laboratory, or field-measurement techniques. Some projects focus on the improvement of existing techniques or part of analytical procedures.

The example selected in this paper shows the necessary evaluation of analytical steps (extraction and derivatization) prior to a certification campaign: the project on tin speciation is one of the first of its kind which was started by the BCR programme in 1987; it followed the usual step-by-step approach (interlaboratory studies of increasing difficulty) which enabled to improve the state-of-the-art of butyltin determinations in sediment[11]. After a series of interlaboratory studies (including two certifications), some question marks, however, remained on the extraction and derivatization efficiencies of the analytical methods currently used. Consequently, an evaluation of extraction and derivatization procedures was decided prior to the tentative certification of butyl- and phenyl-tin compounds in a mussel sample (candidate CRM 477).

An evaluation of extraction variables for the recovery of naturally bound butyl- and phenyl-tin compounds from a marine sediment has been carried out in a first stage. Extraction was performed by sonication at atmospheric pressure. The following extraction variables were optimized: i) acid hydrolysis (time and acid strength); ii) solvent polarity (n-hexane, toluene and HOAc); iii) extraction time; and iv) type of complexing agent (tropolone, diethyldithiocarbamate).

Alkylation with various Grignard reagents and ethylation with sodium tetraethylborate have been compared and optimized. Parameters controlling the yield of the Grignard derivatization such as time and temperature of reaction, effect of shaking and reagent concentration were studied. Efficiency of different Grignard reagents, including methyl-, ethyl-, propyl-, pentyl-and hexyl-magnesiumbromide was tested as well. Ethylation with sodium tetraethylborate was optimized by studying the influence of reaction time, pH of the medium, and reagent concentration. The derivatization study was performed on homogenised mussel samples; final determinations were by GC-FPD and/or GC-MS.

The results of this study will be of high importance for the certification of the candidate CRM 477, i.e. thorough recommendations will be summarized and distributed to the participants; this information will be made available in the certification report.

Network to Harmonize Leaching/Extraction Tests[12]

As mentioned above, the adoption of a standard requires in most cases that the proposed standardized method(s) be assessed through interlaboratory studies.

One approach consists in preparing reference materials to be analysed by a group of expert laboratories from different EC Member States and to possibly improve or adopt the method on the basis of the results obtained. In some cases, CRMs certified for operationally-defined parameters (following a standardized method, e.g. single or sequential extraction) may be prepared for the quality control of the measurements. The SM&T programme provides support to the production of technical evaluation of proposed standardized methods on which basis official bodies such as CEN/CENELEC, ETSI etc. will discuss the adoption of a standard.

In this paper, the pre-normative aspect is examplified by a network dealing with the harmonization of leaching/extraction tests: the justification for starting a network on the harmonization of leaching/extraction tests for environmental risk assessment has been discussed in detail in a workshop held in Maastricht in June 1994[13]; it stems for the increasing use of leaching or extraction test methods in different areas, e.g. waste treatment and disposal, incineration of waste, burning of waste fuel, soil clean-up and reuse of cleaned soil, sludge treatment, use of composts from different sources, and use of secondary raw materials in construction; this may lead to the development of a large number of very similar tests in the different fields which will not allow the comparability of data to be achieved owing to their operationally-defined character.

In view of these developments, efforts are needed to harmonize leaching procedures that could be adapted to different matrices, and to validate the use of existing tests in other fields. The development of an even wider variety of leaching tests methods for different matrices is undesirable from a regulatory point of view and for industry. In regulations on environmental impact for disposal, re-use or transport of materials, the boundary lines between fields are not always clear, which can be further complicated by different testing requirements. A material may be a waste in one circumstance and a useful secondary material in another. The aims of the network on harmonization of leaching/extraction tests are the following:

- to harmonize the approaches in existing leaching tests and tests to be developed in the fields of soil, sediments, sludges, waste, stabilized waste and construction materials;
- to exchange information among different fields and define the problems in specific areas;
- to facilitate the development of a generic approach to leaching by intensive consultation of experts working in different fields. From the evaluation of the needs in specific fields, an attempt will be made to build a common strategy for the use/validation and interpretation of leaching/extraction tests to assess and optimize environmental properties of materials in a variety of applica-

tions. This will at least provide a link between the leaching/extraction tests in different fields such that results from one field can be related or linked to that in other fields;

- to form a network of experts in the fields of waste treatment and disposal, soil cleanup, soil use, and materials in construction to disseminate information through a newsletter;
- to formulate recommendations for the implementation of more generally applicable approaches in the evaluation of leaching results in different fields and define the research needed to resolve specific issues.

The following matrix types are covered:

Waste: bulk wastes, stabilized wastes, chemical wastes, inert wastes, vitrified wastes Soil: natural soil, contaminated soil, compost Sediments: natural sediment, dredged spoils Sludge: industrial sludges, sewage sludges, water treatment sludges Construction materials: concrete, aggregates, bricks, composites, tiles, wood (impregnated), drinking water pipes.

The enquiry for interest has led to more than 350 responses which have been included in a database for distribution of further mailings of the newsletter (available free of charge).

Proficiency Testing for the Quality Assurance of Marine Monitoring[14]

QUASIMEME (Quality Assurance of Information from Marine Environmental Monitoring in Europe) aims to improve the quality of data of laboratories which submit their results in European Marine Monitoring programmes (e.g. the monitoring programme carried out in the context of the Oslo and Paris Commission). The first step in this programme focused on the analytical quality assurance through a series of stepwise learning programmes (interlaboratory studies with samples chosen to investigate particular aspects of analytical procedure(s)) combined with workshops in which the sources of error were identified and discussed. The programme emerges into a proficiency testing scheme on a subscription basis. All laboratories involved or interested in marine analysis can subscribe to this scheme.

About 90 laboratories took part in the QUASIMEME project. A total of about 50 determinands were studied in different matrices (seawater, marine sediment, marine biological tissues). About 60.000 data were collected, corresponding to an average response of the laboratories of ca. 70%.

Many laboratory-performance studies invoke the standard ISO 5725 for the statistical evaluation of the data. The QUASIMEME project decided not to use this standard considering that ISO 5725 was designed for method-performance studies (i.e. containing assumptions adapted to such studies) and not for laboratory-performance studies. In particular, ISO 5725 assumes that normal distributions underlie the within- and between-laboratory variances and that all within-laboratory variances are equal. These assumptions are not valid for a large international study in which a wide variety of methods and equipment are employed for trace level determinations. In addition, the outlier tests used are subject to debate.

Robust statistics were chosen for the evaluation of the QUASIMEME data; this approach does not impose any assumptions regarding distributions and does not use any outlier tests. Robust statistics were actively promoted in the period at which the QUASIMEME project has started. Two implementations of robust statistics were tested: the method proposed by the UK-Analytical Methods Committee and the algorithm described by Lischer. In practice, the application of robust statistics was not without problems. The distributions encountered for many determinands were skewed, tailing towards higher concentrations. This tailing was often related to analytical problems (e.g. contamination, poor selectivity/specificity), but also dilution-, calculation- or transcription errors which played an important role. The latter was inferred from a magnitude of data which were a certain factor too high (e.g. 2, 10 or 1000). The robust statistics algorithm invokes a procedure in which data which fall outside a certain window (the median +/-C.S, where C is a constant and S is the robust standard deviation) are substituted with the concentrations delineating the window. In the case of distributions which tail to e.g. higher concentrations, a proportionally large amount of data will be downweighted, giving rise to large cluster of data at the higher limit, and thus overestimating the robust mean. The data were, therefore, always inspected prior to a statistical calculation. Data which were declared as obvious outliers, e.g. with Z-scores greater than 6, were removed from the dataset before the calculations were carried out.

Another problem which hampers all methods for statistical evaluations was that in some cases bimodal distributions were observed. This was specifically the case for the determination of metals in sediments, where "total" (e.g. determinations performed by neutron activation analysis or HF-digestion followed by instrumental analysis) or "partial" (e.g. aqua-regia digestion followed by instrumental analysis) methods were used. In such cases, the datasets were evaluated separately for the "partial" and "total" methods. The robust means and standard deviations were used to estimate whether the difference was significant. If this was the case, the datasets were evaluated separately; otherwise, the data were combined and the assessment was carried out using one robust mean and one assigned value.

The Z-scores advocated by the ISO/IUPAC/AOAC protocol for laboratory performance studies was used. It proved to be an elegant, clear way to indicate the performance. The project used a target standard deviation of 6% for the calibrant solutions and 12.5% for real samples.

The assigned values were obtained in different ways. For calibrant solutions and the nutrient samples, the nominal concentrations were known and these concentrations were used as assigned values. For the real samples, the concept of "reference laboratories" was used, i.e. laboratories with quality systems and a proven track record in certification campaigns organised in Europe or North America. At the beginning of the project, laboratories external to the project were invited as reference laboratories; during the development of the project, it became clear which participants performed at such a level of quality that they could be designated as "reference laboratory" so that no external laboratories were anymore needed. The data of the reference laboratories were critically assessed. Frequently, data had to be discarded on the basis of expert judgement. The robust mean of the remaining data was used as assigned value; as an additional control, a comparison was always performed with the robust mean of the participants.

Several difficulties were encountered in the process of establishing assigned values. In some cases, the robust mean of the participants differed strongly from the nominal value of calibrant solutions. This was the case for Hg in the first round and for PAH calibrant solutions. In such cases, the question arose whether the assigned values should be adjusted. In all but one case, the nominal values were maintained after careful scrutiny of all data. An unexpected observation was made for Cu in marine sediment. In this case, the results of the three reference laboratories (all using "total" methods) differed largely from the robust mean of the data reported by the participants using "total" methods, whereas a good agreement was observed with the data reported by the laboratories using "partial" methods. The reference laboratories had a good agreement with different analytical techniques. Therefore, the assigned value derived from the reference laboratories was maintained. No explanation for the deviations observed could be found, even after a technical discussion among the participants. It appeared, finally, that the performance of the reference laboratories was not stable, e.g. for CB analysis the performance decreased during the project which was ascribed to the increasing workload of these laboratories.

The uncertainty in the assigned values was a third problem which had to be overcome. In the first round of interlaboratory studies, extremely low contents of Hg and Cd in a sandy marine sediment were encountered. The between-laboratory variance of both participants and reference laboratories was high. In this case, the target standard deviation was maintained. Following an inspection of two-sample plots, it was decided, however, to judge Z-scores up to 4 as satisfactory. This approach had the disadvantage that Z-scores were given a different meaning for different samples. In the last round, it was decided to modify the target standard deviation, defining the latter as the minimum of (12.5% of the assigned value, the standard deviation (as %) of data of the reference laboratories).

A number of conclusions were drawn:

- Robust statistics require to be applied with just as much care as conventional statistical techniques. The nature of the distribution underlying the data needs to be assessed. For skewed distributions, incorrect robust means will be calculated when no precautions are taken.
- The Z-scores appear to be an elegant way to summarise laboratory performance.
- Establishing assigned values requires expert judgement.
- The uncertainty in assigned values may be accounted for by replacing the target standard deviation in the formula for the Z-score by the uncertainty when the latter becomes the greatest.

Additional Information

The programme publishes an information bulletin, the "Measurements and Testing Newsletter", which can be obtained free of charge (please contact Ph. Quevauviller at the SM&T programme). Further information on the certified reference materials produced (catalogue and price list) by the SM&T programme can be obtained at the Institute for Reference Materials and Measurements, Management of Reference Materials Unit, Retiesweg, B-2440 Geel. (Fax: +32-14. 590406)

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