

# Can plasma spectrochemistry assist in improving the accuracy of chemical analysis?

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## Abstract

The validity of data produced in chemical analysis must be properly guaranteed for their quality as analytical results are far from being accurate. There is a growing pressure to improve the overall quality of analytical information and to make it consistent with general metrological principles.

Plasma spectrochemical methods are evaluated in their ability to increase the accuracy of analysis, to serve eventually as definite methods of analysis and to assist in the elaboration of certified reference materials. Possibilities reside in the application of isotope dilution mass spectrometry and in increasing the knowledge of the fundamental processes governing ion and photon formation so that they become able to describe fully the processes which link analytical signals with concentration. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

At present there is a growing pressure to improve the overall quality of analytical information and to make it consistent with general metrological principles. Demonstrating the validity of chemical measurements (analytical data) is a prerequisite for achieving the mutual recognition and comparability of chemical analyses.

Chemical analysis is a particular measurement process, distinct from physical measurement processes. The analytical act is an indivisible process including various sources of errors occurring in sample treatment and other preliminary operations of the analytical process, the measurement equipment, the measurand

in its relation to the particular environment (the sample subjected to analysis) and the mostly complex overall procedure that leads to the final result. Various errors in the determination depend on random error sources in sampling, sample preparation for analysis, storage of the sample and in chemical separations and measurements. The quality of the results depends also on systematic sources of error such as incomplete recovery and other losses of the measurand and contamination. Analysis based exclusively on a measurement is extremely rare in practice: it is limited to some rather exceptional methods of non-destructive instrumental analysis.

In its applications, analysis is also very strongly dependent on the properties and the overall composition of the samples involved; results obtained by instrumental analytical methods are influenced by matrix effects. Thus, analytical procedures and the measurement standards used are very often quite different

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when applied to different types of samples. Therefore, processes of method validation need to be related to the overall analytical act and to the specific sample involved in order to cover errors due to sampling, incomplete recovery of the analytes, contamination, reagent blanks and interferences. This is commonly achieved by studies of all parameters affecting the analysis on one side and, on the other side, by validation of the methods by inter-laboratory or inter-method comparisons, the use of reference samples, proficiency testing and other practical and operational validation tools.

There is a widespread belief that, all too often, analytical results are far from being accurate and that these inaccuracies do not occur only on the borderline of discipline (application of new methods under development), but also during the application of well established methods. It is tempting to attribute most of the problems to the measurement process and then the introduction of more metrology in analytical chemistry could improve this situation in order to restore, as is claimed in one paper, “law and order!” for such measurements [1].

In the fields of physical measurements (length, voltage etc) straightforward calibration procedures ensuring direct traceability to national and international calibration systems are generally applicable. In chemical analysis calibration and traceability to the SI is, however, considerably less obvious. The underlying concepts originating from metrology i.e. measurement science, tend to reduce or simplify the analytical practice to the measurement part of the analytical process. As discussed earlier in this paper, the measurement step is only one, often minor, part of the entire analytical process, among many other important parts that contribute to the overall bias on the results and to the confidence limits. Besides the number of different situations encountered in chemical measurements is bewilderingly large compared to the situation in other measurement processes.

The basic concepts behind traceability in chemical measurement (analysis) have been implemented in practice by the Consultative Committee on Quality of Measurements (CCQM), a consultative Committee of the International Conference of Weights and Measures (CIPM), established in 1993 to translate traceability concepts to chemical analysis. The central items addressed by CCQM are concerned with methodologies (primary methods of measurement) and

organisation (reliance on metrological reference laboratories). Primary methods of measurement are methods that provide a direct link to the SI. These methods are completely described and understood and imply that a complete uncertainty statement can be expressed in terms of the SI units *without reference to a standard of the quantity being measured*. The requirement that no comparative measurements are allowed is consistent with the basic aim of coupling the method’s results directly or indirectly to the SI unit system. This excludes, however, nearly all of the available instrumental analytical techniques (including any plasma methods) from being considered as a primary method, leaving a very limited number of methods with the potential of being considered as such. At present these are isotope dilution with mass spectrometry (IDMS), coulometry and differential scanning coulometry, gravimetry and titrimetry, determinations based on the lowering of the freezing point and based on the theorem that in sufficiently dilute solutions the solvent behaves ideally. In addition, the use of these primary methods is restricted to determinations in pure or simple compound systems (samples not containing impurities that potentially act as interferences and hence, could become an error source).

Several comments can be formulated on these concepts [2]:

- Considering the limitations in available primary methods, emphasis must be placed on other measurement standards. For determination involving non-isolated substances, i.e. those present in complex matrices, reference materials are needed which are firmly linked to the SI units by using the primary methods. In practice, this implies that such reference materials must be artificially produced e.g. by mixing them together from the reference materials made using the primary methods. This distinguishes them from any real-life reference materials or “matrix” reference materials based on natural (non-synthetic) samples. Many instrumental methods of analysis, on the other hand, rely on matrix type references for calibration and quality control as synthetic reference materials are inappropriate for a variety of reasons.
- Traceable certified reference materials (CRMs) relying on primary methods are only available in exceptional circumstances as the exclusive use of

primary methods of measurement for making them is impossible in practice [3]. For trace element determinations, the National Institute of Standards and Technology (NIST) relies whenever feasible on the use of methods such as IDMS for NIST standard reference materials (SRMs). In the EU there is also a growing pressure to include primary methods for the certification of CRMs.

- Many of the important developments in modern analytical chemistry are completely out of reach with the primary methods as defined now: e.g. speciation analysis, ultra-trace analysis, microscopic and surface analysis. It is certainly not an overstatement that actual needs of analytical chemistry go far beyond the problems addressed up to now in discussions on metrology and traceability of chemical measurements. King [4] states that it is necessary to build bridges between the metrology and analytical chemistry cultures to construct a system of chemical metrology which addresses the real problems of analytical chemistry and provides support to the routine analytical laboratories at a price they can afford.

## 2. Two examples

All these problems form the basis of a number of misunderstandings of the analytical chemistry community towards the ideas put forward by metrologists. The following examples will illustrate some of the points made.

### 2.1. The use of primary methods in a certification of bronze alloys

Within a 4th Framework Programme Project of the EU, work was done on the certification of five bronze

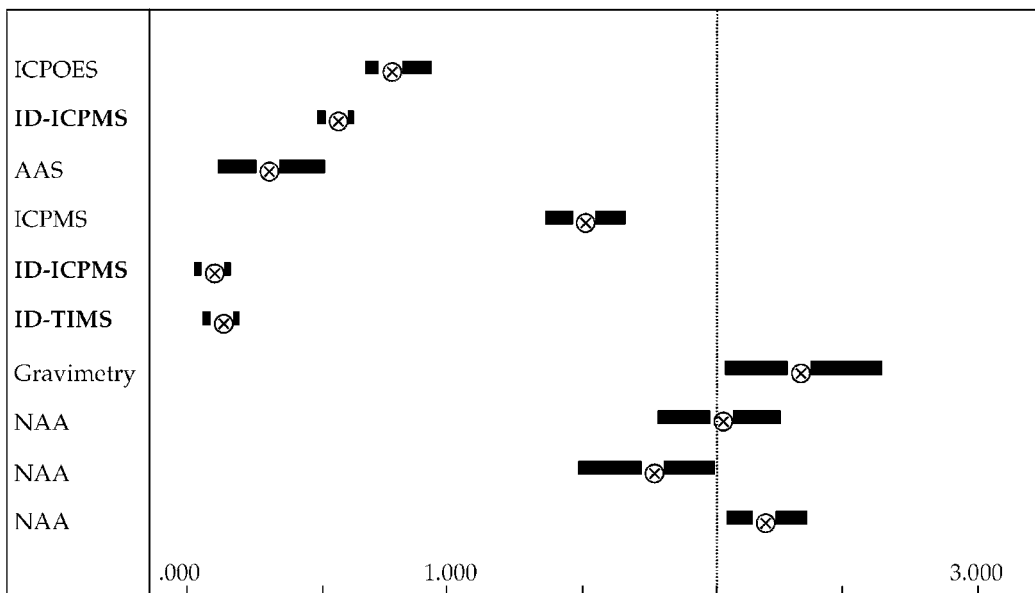
alloys corresponding to composition of the major archaeological bronze compositions [5,6]. The motivation behind the development of these CRMs was to be able to use them as calibrants for energy dispersive X-ray fluorescence spectrometry, which is a preferred method for non-destructive analysis of archaeological bronzes, particularly in the field i.e. on the site of an excavation or within a museum environment. The overall composition of the certified elements of the five alloys of this study is shown in Table 1 [5]. The alloys were carefully made by powder metallurgy techniques involving cold and hot isostatic pressing in a strictly controlled process from stoichiometric amounts of the alloying elements. The concentration levels of the alloying elements to be certified are on the percentage level.

A number of methods were employed in the certification, such as gravimetry, instrumental neutron activation analysis, atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP AES), inductively coupled plasma mass spectrometry (ICP MS) and thermal ionisation mass spectrometry (TIMS). The latter three methods were applied allowing the use of isotope dilution mass spectrometry (IDMS).

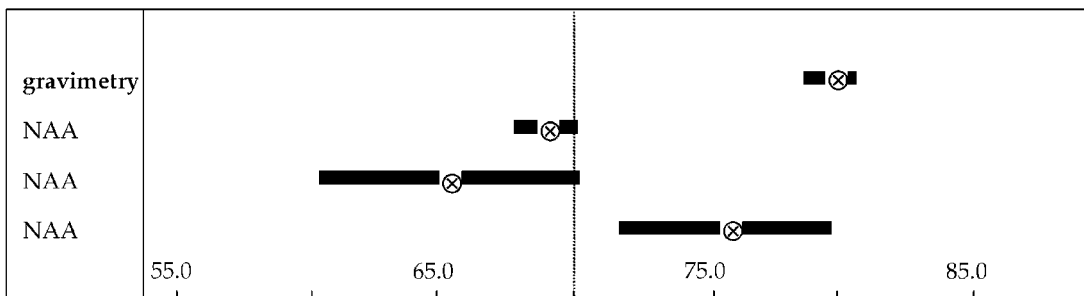
In what follows we will concentrate on the results of the determination of the alloying elements. Gravimetry and IDMS were applied in order to include primary methods in the certification exercise. Problems resulted with the application of these primary methods as is shown in Fig. 1. Results of IDMS and gravimetry for tin did not correspond with either the previous information of the samples or the results obtained with the other methods of analysis. Precipitates of tin were observed when dissolving the bronze samples, most probably due the presence of oxidised tin in the alloy. The three different IDMS results, obtained by

Table 1  
Certified values and uncertainties ( $ku_c$ ) for CRM 691 in  $g\ kg^{-1}$  [5]

Element	Identification				
	A	B	C	D	E
Certified values $\pm ku_c$ ( $g\ kg^{-1}$ )					
As	$1.94 \pm 0.10$	$0.99 \pm 0.10$	$46.0 \pm 2.7$	$2.85 \pm 0.22$	$1.94 \pm 0.20$
Pb	$78 \pm 7$	$3.9 \pm 0.3$	$1.75 \pm 0.14$	$92 \pm 17$	$2.04 \pm 0.18$
Sn	$71.6 \pm 2.1$	$20.6 \pm 0.7$	$2.02 \pm 0.29$	$101 \pm 8$	$70 \pm 6$
Zn	$60.2 \pm 2.2$	$148 \pm 5$	$0.55 \pm 0.05$	$1.48 \pm 0.24$	$1.57 \pm 0.25$



(a)



(b)

Fig. 1. (a) Results of tin determination in composition C of CRM 691 in  $\text{g kg}^{-1}$ . (b) Results of tin determination in composition E of CRM 691 in  $\text{g kg}^{-1}$ . The length of a horizontal dotted bar corresponds to one standard deviation of the set of data. The vertical dotted line features the nominal value.

ICP MS and TIMS appeared to be systematically low (Fig. 1a), apparently because of a lack of isotopic equilibrium between the spike and the sample. In the case of the use of gravimetry for the determination of tin, co-precipitation of antimony provided systematically too high results (see Fig. 1b).

The conclusion is that, despite their status as a primary method of measurement, neither IDMS nor

gravimetry could be considered for the certification as both were prone to error sources when used in a practical analytical determination, equilibrium exchange problems or contamination, respectively. This conclusion should not be interpreted too strongly. As will follow later, IDMS is one of the most powerful means of validating analytical results; there are numerous examples in the literature in which its application demonstrates the usefulness for certification.

## 2.2. The certification of methyl mercury compound in environmental samples

The recognition of the fact that the determination of the level of a total metal or of a metalloid is not sufficient to evaluate its impact on the environment, its bioavailability and its toxicity has stimulated the development of species-selective analytical methodologies during the last decade. The question how to access this molecular information (speciation) has become one of the most crucial, pertinent and challenging issues of the recent analytical chemistry because of its impact on environmental chemistry, eco- and clinical toxicology, medicine, food and energy industries [7].

A number of hyphenated techniques have been used in many environmental and biomedical studies based on the combination of gas chromatography with AAS (GC–AAS), microwave induced plasma AES (GC–MIP AES) and ICP MS (GC–ICP MS).

Advances over the past years have brought the instrumental detection limits to the sub-pg level on a routine basis. The community bureau of reference (BCR) organised a number of intercomparison studies that convincingly demonstrated the reliability of the procedures developed. On the basis of these results a number of CRMs were developed for these compounds in various sediments and tissues [8]. Overall, they are fit for the purpose: the availability of the CRMs or reference materials allows laboratories to validate their analytical procedures.

One of the CRMs developed by the BCR is the matrix type CRM 580 with a certified concentration of methyl mercury in estuarine sediment. The results of the laboratories and methods participating in the certification are shown in Fig. 2. There are similar reference samples e.g. IAEA-356 (methyl mercury in polluted marine sediment) developed by the International Atomic Energy Agency (Vienna, Austria).

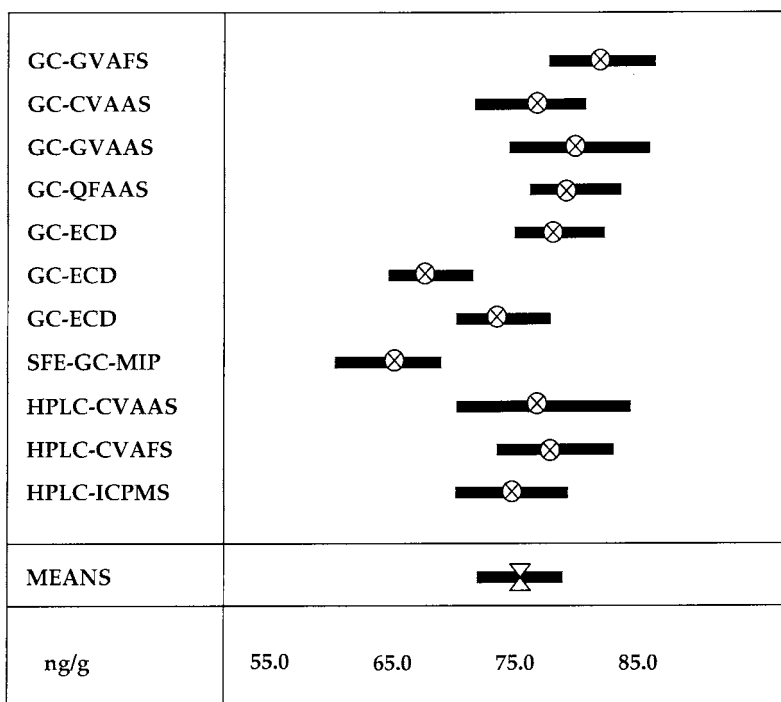


Fig. 2. Results of methyl mercury determinations in estuarine sediment, CRM 580. All results are six replicate determinations using various methods. Means is the mean of laboratory means with 95% confidence interval or certified value and its confidence interval (95%). (adapted from [11]). Abbreviations: CVAAS, cold vapour atomic absorption spectrometry; CVAFS, cold vapour atomic fluorescence spectrometry; ECD, electron capture detection; MIP AES, microwave induced plasma atomic emission spectrometry; QFAAS, quartz furnace atomic absorption spectrometry; SFE, supercritical fluid extraction; GC, gas chromatography.

The reason for the development of these materials resides with the extreme toxicity of methyl mercury and its ability to bio-accumulate in fish tissues, which necessitates monitoring of the compound in the environment.

The procedures for the determination of this compound involve a succession of different steps and all of them may be prone to systematic errors. Concerns were expressed on the possible formation of methyl mercury from inorganic mercury during steps in the analytical procedures, especially during distillation or hot acid extraction [9,10]. The formation of these can lead to positive errors and has been studied by IDMS and conventional analytical techniques.

On all these there was a discussion in the form of letters-to-the-editor of "Analytical Chemistry". One side of the argumentation developed the viewpoint that the certification status of CRM-580 and other current CRMs on methyl mercury should be revoked and replaced with a "consensus value, probably biased high". The authors state that "the standards and certification community perpetuates the superiority of precision over accuracy" [11]. The opponent argument was formulated that the CRM 580 was developed on the basis of results of a number of laboratories with an outstanding performance and with validated analytical techniques. The artefact and its effect on the analysis was carefully taken into account and, hence, it was claimed that CRMs should not be doubted on the basis of some suspected risks of systematic errors in one particular technique [12].

It follows from this that there are two ways to view a problem such as this one. Seen as extremes the first viewpoint is dogmatic and the second pragmatic and both have their respective truths. Laboratories, however, badly need reference materials to obtain the best comparability. The accuracy of CRMs can always be questioned, there are consensus values and they may be biased to some extent. When this bias is detected it is the responsibility of certification organisations to take a proper action to investigate or remediate the problem. This is what happened with CRM-580 as a workshop was organised to review the specific problems with methyl mercury artefacts (Wiesbaden, Germany, May 1998) [13]. In the meantime, despite formal arguments that interlaboratory comparisons cannot establish traceability [14], one tends to believe

that CRMs are the best way for laboratories to verify the performance of their methods.

### 3. Plasma methods for accurate analysis

The evolution in plasma methods is in the direction of MS as there is a general trend away from optical plasma methods to mass spectrometric detection [15].

#### 3.1. Precision and accuracy

In general, it is not the magnitude of the variation in sensitivity and the matrix dependence which are of importance for quantitative analysis but the possibilities to transfer the ion intensity data to real concentrations without the need to dispose of standard samples which are closely comparable to the unknown in composition and structure.

A general phenomenological way for describing the deviations between the recorded mass spectrum and the solid sample composition consists in the use of relative sensitivity factors (RSFs) defined as:

$$\frac{I_x}{I_y} = \frac{C_x}{C_y} \text{RSF} \left( \frac{x}{y} \right)_z$$

in which  $I_x$ ,  $I_y$  and  $C_x$ ,  $C_y$  are measured ion intensities and concentrations and the suffixes are for unknown element  $x$ , and internal standard  $y$ , and matrix  $z$ .

The particular value of an RSF characterises the dependence of the sensitivity of an element  $x$  in a given matrix  $z$ . It includes all the discrimination effects present under given experimental conditions in the ion source, the mass spectrometer and detection system. In practice, these factors can be determined by analysing standard samples. Today, after many years of debate, it is still an open question whether it is possible to estimate or determine them from a priori physical and chemical considerations.

Within the range of available methods some respond closely to the ideal analytical situation in which RSFs approach unity for every element in any matrix. They approach the situation of an absolute quantitative analytical method in which the only a priori assumption to be made is the concentration of one single constituent, often a matrix species whose concentration is known from bulk analysis or from stoichiometric considerations. This comes close to the definition given

for a primary method of measurement. Other methods are prone to matrix dependent variations in sensitivity that vary over several orders of magnitude. Especially SIMS provides quite large variations in RSFs although this can be remediated by post-ionisation as in secondary neutral MS.

RSFs are the result of different processes taking place in sequence: atomisation, ionisation, plasma expansion, ion beam formation, mass discrimination in the spectrometer and finally detection. Quantitative analysis relies on the proper understanding of at least the most important of the discrimination processes taking place, so that it becomes possible to take them into account for quantification.

The theoretical understanding of RSFs includes efforts to establish correlations between basic material parameters of the matrix and the analyte and the sensitivity coefficients themselves. Such correlations have been demonstrated with the enthalpy of sublimation, the atomisation energy, the ionisation potential, the covalent radius, the vapour pressure and the atomic mass by Van Hoye et al. [16] and the late Gregory Ramendik [17]. Another approach is to follow time dependent ion distributions in the expanding plasma and relate the ion production for different elements to

their relative sensitivity coefficients [18,19]. Such approaches for quantitative analysis based on a limited set of parameters reduces inaccuracies to 30% at trace levels [20]. The practical value of this and other approaches lies with the fact that they can be used to systematise large data set and reduce substantially the systematic errors of analyses without reliance on reference materials.

Many data are available for multi-component samples to show that RSFs obtained for glow discharge mass spectrometry (GDMS) exhibit the favourable conditions for accurate measurements. From one matrix type to another the RSFs expressed as relative ion yields seem to be quite uniform with a matrix dependence of about 30% as is shown in Fig. 3 [20,21]. Compared to other ion sources for solids its major advantage is that the two main contributing processes in the source (vaporisation/atomisation and ionisation) are effectively decoupled in one simple and stable ion source which can be optimised independently for optimum performance [22]. This leads to source conditions that are relatively free from matrix effects. Laser ablation for sampling and atomisation coupled to ICP MS as an ionisation source is also a potentially powerful method to achieve high accuracy analysis [23].

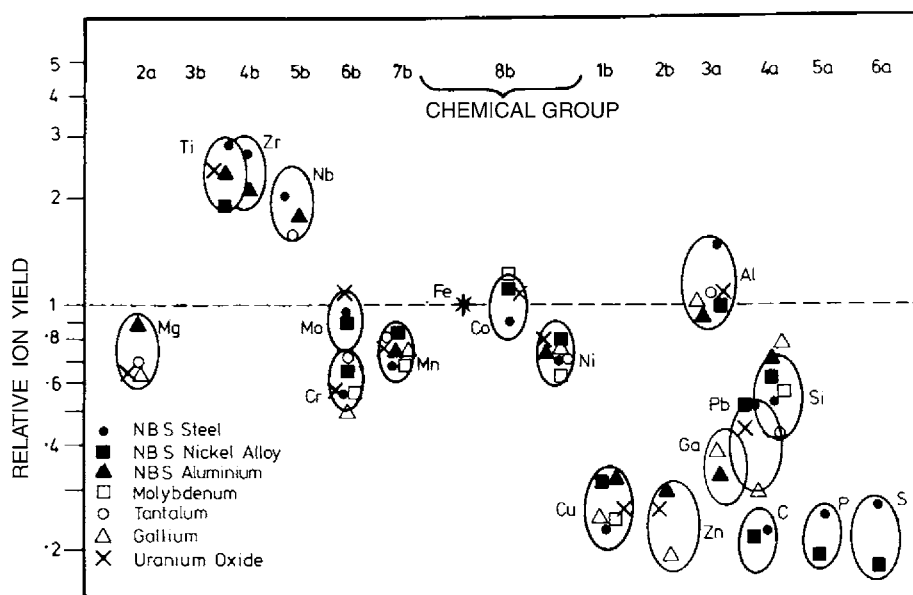


Fig. 3. Relative ion yields in GDMS for different matrices [21].

Valuable as such approaches may be for good analytical practice, a more thorough insight in the basic plasma processes is desirable as well as the use of plasma diagnostics [24]. This might enable to find a correlation between some plasma properties and the analytical characteristics, and it may be helpful to improve the analytical characteristics (accuracy, precision, detection limits) by changing the plasma conditions.

### 3.2. Modelling of analytical GD plasmas

Insight in the plasma processes can be obtained by numerical modelling or by plasma diagnostics. In the following, we will give some more information about models for glow discharges, as an example of how numerical models can assist in better analytical practice.

Glow discharges are used in analytical chemistry but also in many other application fields, such as semiconductor industry (for etching of surfaces or the deposition of thin films), materials technology (e.g. for the deposition of hard, protective coatings), as lasers or light sources or in flat plasma display panels [25]. In the plasma physics literature, a large number of models are available to describe these “technological” glow discharge plasmas (see [25]), but the number of models presented for analytical glow discharges is rather limited (e.g. [26–31]). The models developed by Bogaerts and Gijbels give a comprehensive picture of the glow discharge. It is a kind of “modelling network,” i.e. a combination of various models (Monte Carlo, fluid and collisional-radiative models) for the

different plasma species: electrons, argon atoms, argon ions, argon atoms in excited levels including the metastables, sputtered copper atoms and copper ions, both in the ground state and in excited levels; see Table 2. Typical results of the models include the electrical characteristics, the electric field and potential distribution, the densities, fluxes and energies of the various plasma species, and information about collision processes in the plasma. Other calculation results, of more analytical importance, are the erosion rates and crater profiles due to cathode sputtering (which is of interest for glow discharge depth profiling), optical emission intensities (of interest for GD-OES), and ion fluxes to the mass spectrometer (relevant for GDMS).

Fig. 4a shows a calculated crater profile after 45 min of sputtering of a copper cathode, in a glow discharge cell of the VG9000 mass spectrometer. It is clear that for good depth profiling (good depth resolution), the crater should be as flat as possible, in order to sample atoms from the same depth. Hence, the crater profile illustrated in Fig. 4a is not very suitable for depth profiling, because it is much deeper at the sides than in the centre. This calculated profile is, however, often obtained experimentally, as is presented in Fig. 4b (for the same conditions as used in the calculations). Indeed, the measured and calculated crater profiles look qualitatively the same (i.e. deeper at the sides than in the centre, crater walls not very steep, small rim outside crater profile, due to redeposition of sputtered atoms), and the absolute values of the crater depth are also in good correspondence. This illustrates that the characteristic crater profiles which are often found

Table 2  
Overview of species assumed to be present in the plasma, and the models used to describe the behaviour of these species

Plasma species	Models
Argon gas atoms	Heat transfer equation
Fast electrons	Monte Carlo model
Slow electrons	Fluid model
Argon ions ( $\text{Ar}^+$ , $\text{Ar}^{2+}$ , $\text{Ar}_2^+$ )	Fluid model
Fast $\text{Ar}^+$ ions in cathode dark space	Monte Carlo model
Fast Ar atoms in cathode dark space	Monte Carlo model
Argon atoms in excited levels	Collisional-radiative model
Sputtering of copper atoms	Empirical formula + energy distribution functions of bombarding species
Thermalisation of sputtered copper atoms	Monte Carlo model
Copper atoms, $\text{Cu}^+$ and $\text{Cu}^{2+}$ ions, in ground state and in excited levels	Collisional-radiative model
Fast $\text{Cu}^+$ ions in cathode dark space	Monte Carlo model



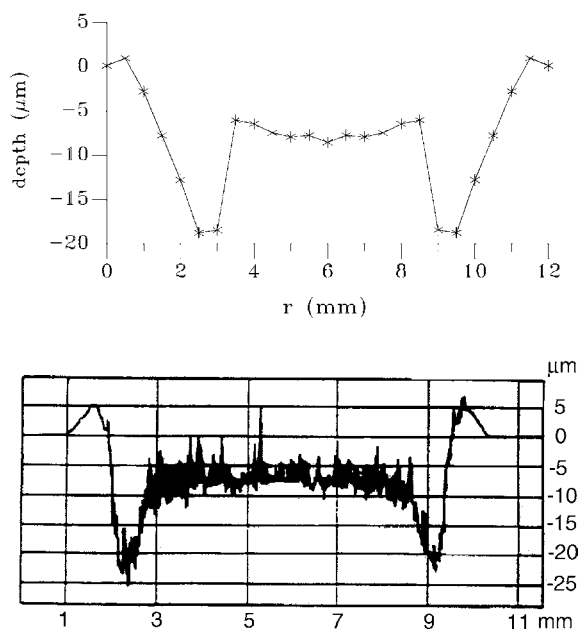


Fig. 4. Calculated (a) and measured (b) crater profiles after 45 min of sputtering of a copper cathode in a glow discharge cell used in the VG9000 glow discharge mass spectrometer, at 1000 V and 3 mA.

experimentally, can be reproduced by the model. Therefore, in principle the model can be used to predict for which discharge conditions (voltage, pressure, current) a more suitable crater profile can be reached, or how the cell geometry has to be changed (e.g. to avoid focussing of the ion fluxes by the electric field lines) to obtain an optimal (flat) crater profile [32].

Because it is possible to calculate the level populations of the argon and copper atom and ion excited levels with the model, the optical emission intensities of various lines originating from these excited levels can also be obtained, which is of interest to GD-OES. Fig. 5a and b illustrates the calculated and measured optical emission intensities of the Cu I 324.7 nm line, as a function of distance from the cathode, at various conditions of pressure and current [33]. It is clear that the calculated and measured data are in very good agreement with each other, both with respect to the behaviour as a function of distance from the cathode, and also for the effect of pressure and current. This suggests that the model gives a realistic picture of the

various populating and depopulating processes for the excited levels, and hence of the optical emission intensities, and can be used for the prediction of optical emission signals in GD-OES.

Recently, there is in GD-OES a growing interest in the effect of small amounts of hydrogen (either H originating from the sample, or H<sub>2</sub> added to the argon gas) on the optical emission intensities of various lines in GD-OES, because this might play an important role for the quantification procedure [34]. This could also be an interesting application for the existing models of glow discharges, i.e. by adding various hydrogen species and chemical reactions to the existing models and plasma species (see Table 2), the effect of hydrogen on the plasma behaviour could be predicted, and a correlation with the analytical behaviour and the optical emission intensities could be made. Recently, an overview has been made of all possible reactions in an argon–hydrogen glow discharge plasma [35]; the authors plan to add the most important chemical reactions to their existing modelling network in the near future.

Finally, as a spin-off, the modelling network described above has also been used to explain experimentally observed differences in RSFs for different elements in GDMS [36]. Based on a systematic investigation for 42 elements of the periodic table, it was suggested that asymmetric charge transfer could explain the differences in RSFs for different elements. Indeed, it appears that transport of the sputtered atoms, as well as ionisation by electron impact and Penning ionisation are more or less the same for all elements, but asymmetric charge transfer is a very selective process, occurring only for those elements which have ionic energy levels available that overlap with the argon ion levels. Exact quantitative prediction of the RSFs in GDMS was, however, not yet possible, due to the lack of accurate cross sections for the various ionisation mechanisms (Penning ionisation, electron impact ionisation, and especially asymmetric charge transfer). This is also true in general: due to the large uncertainties in the cross sections and other data necessary for the models, the latter yield mostly only qualitative results (e.g. predictions of certain trends when changing the plasma conditions). Quantitative predictions, e.g. in order to really improve the accuracy of the analytical measurements, can however mostly not yet be expected.

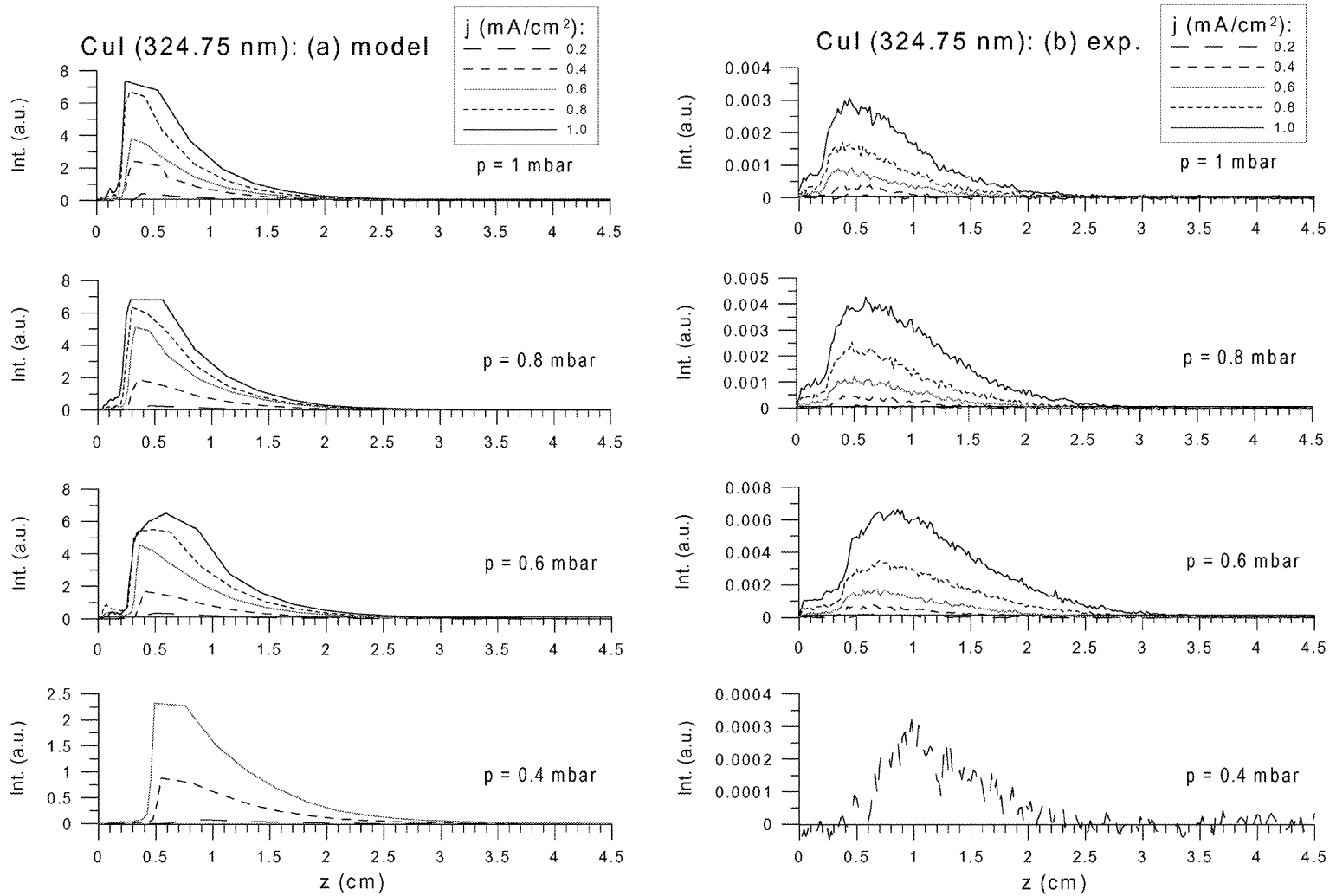


Fig. 5. Calculated (a) and measured (b) optical emission intensities of the Cu I 324.7 nm line, as a function of distance from the cathode, at various conditions of voltage, current and pressure.

### 3.3. Isotope dilution mass spectrometry

Example 1, in which the results obtained by IDMS were demonstrated to be inappropriate for certification purposes, should not be interpreted wrongly. Isotope dilution analysis (IDA) in general and IDMS in particular is a remarkable aid in improving the accuracy of elemental and molecular analysis. The advantage of IDMS can be summarised as follows.

- IDMS is a primary method of measurement and as such is able to provide reliable and precise SI traceable results if used as a method for measurement (but not necessarily as a method of analysis).
- Instrumental parameters do not influence the method's result and by building the measurement of isotope ratios in the analysis, losses due to separation or preconcentration are allowed. The accurate measurement of isotope ratios after the addition of species specific spikes also allows the study of interfering phenomena (e.g. the difficulties in the example of methyl mercury determinations given before). It can hence be exploited as a quite valuable help in definite methods development.

The precise and accurate measurement of isotope ratios is important in many application fields (isotope variations in nature, dating, nuclear industry, tracer experiments, etc.).

It appears that the dominant technique for precise isotope ratio measurements, TIMS, is now being complemented by plasma methods, particularly by ICP MS [37]. None of the plasma methods can match TIMS when it is equipped with multi-collector ion detection as it allows a long-term precision down to 0.002% [38]. The reasons for the introduction of alternative methods is the non-general applicability (TIMS being difficult for elements with a high ionisation potential), speed, convenience and multi-element sensitivity.

The potential of ICP MS for isotope ratio measurements is well recognised. It provides ease of operation and high sample throughput. The development of ICP MS for isotope ratio measurements is now in full progress, the major drawbacks on reaching accuracy and precision being now attacked by several developments. The precision of isotope ratio measurements with quadrupole ICP MS approaches 0.1% in the most favourable conditions (0.2–1% for ratios involving an isotope with low abundance). Sector magnetic

instruments improved these figures by a factor of 10. Multi-collector measurements for simultaneous high precision measurements provide R.S.D.s in the range 0.005–0.002, hence comparable if not equivalent with those of TIMS. Time-of-flight ICP MS is an important new development for isotope ratio measurements of transient signals such as those obtained in hyphenated methods or laser ablation. Preliminary results indicate R.S.D.s of the order of 0.05% [39,40]. Accuracy is increasingly becoming a crucial issue, therefore, it is important to correct for spectral interferences, mass bias and dead time by calibrating abundance ratios by isotopic CRMs. The introduction of collision cells in ion trap and quadrupole instruments for removing interferences is also being developed [38].

IDMS has been used in a number of elemental determinations in various matrices increasing the method's accuracy. Its use is especially significant for speciation analysis. IDA offers clear advantages over other determination techniques for trace metal speciation e.g. for organometal determinations [41]. In the first place, derivatisation, clean-up and extraction procedures do not need to be quantitative and recovery corrections are unnecessary (provided isotope equilibrium is established). Second, rearrangement reactions between the different species, such as the ones discussed in the example 2, can be detected and studied. Procedures are available for the synthesis of isotopically labelled organometal compounds e.g. dibutyltin (DBT) with enriched  $^{118}\text{Sn}$  [42]. Until recently enriched organometal standards were not commercially available but several sources are now announced. Table 3

Table 3  
Concentration of dibutyltin (DBT) in sediment reference materials found by isotope dilution mass spectrometry at 95% confidence interval using Sn-enriched DBT (adapted from [41])

Sample	Concentration certified ( $\mu\text{g g}^{-1}$ )	Concentration found ( $\mu\text{g g}^{-1}$ )
PACS-2 Individual results	$1.09 \pm 0.15$	$1.015 \pm 0.04$
		$1.13$ (0.9% R.S.D.) <sup>a</sup>
		$1.16$ (0.7% R.S.D.)
		$1.17$ (0.7% R.S.D.)
CRM-462 Individual results	$65 \pm 8$	$61.8 \pm 10.5$
		$56.2$ (1.0% R.S.D.)
		$62.8$ (0.1% R.S.D.)
		$66.4$ (0.7% R.S.D.)

<sup>a</sup> Based on three determinations.

shows results obtained by the application of IDA and ICP MS for DBT in several reference materials [41]. Other applications of IDMS include the determination of chromium species [43]. A US patent was issued for one approach for using isotope dilution not only for the increase of precision but also for the measurement of species conversion [44].

### 3.4. *The analysis of solids: laser ablation MS*

Inter-element fractionation in laser ablation ICP MS (LA-ICP MS) is the most important effect affecting the accuracy of in situ trace element analysis of solid samples. Despite a number of studies (see e.g. [45]), the effects that govern the laser–solid interaction process remain poorly understood. The laser interaction depends on numerous variables related to the laser, the sample and the atmosphere above the sample [46]. First, there are the energetic conditions of the laser (wavelength, energy density, spatial and temporal conditions), second the conditions of the sample (absorption characteristics, thermal conductivity, heat capacity, heat of vaporisation, etc.) that determine crater size, depth and other characteristics on one side and fractionation effects on the other. In addition, there are the complications arising from the fact that the removed material is carried away to the ICP torch as particles of widely variable size.

It should be clear from the foregoing that at present LA ICP MS must rely heavily on reference materials and the RSFs obtained through them for calibration. The method does not match at present the method mentioned in example 3 for accurate determinations. The best accuracy is obtained when fractionation of the element of interest is similar to that of an internal standard [46]. The energy of the laser–solid interaction is certainly a most important factor and the evolution in the technique is to move to shorter wavelength UV laser pulses either the Nd YAG laser at 266 nm or an excimer laser at 193 nm [47].

## 4. Conclusions

Accuracy in chemical analysis has less to do with the measurement process itself than with the entire

procedure of analysis, including all the error sources in sample treatment and preliminary operations prior to the start of the analysis. It is clear that it is needed to increase the quality of the data as produced. Metrological concepts are important for this, but they cannot alone provide an answer to the problems facing analytical chemistry today. The pursuit of accuracy in chemical analysis is a matter of quality assurance, in the laboratory and in the system, less one of the concepts of traceability alone.

Quality control of the laboratories depends on the availability of CRMs, round robin studies, intercomparison and proficiency tests between methods and between laboratories. In all this, due to the wide applicability, plasma methods are of special importance. Isotope dilution is defined as a primary method of measurement but this does not mean that it is a fail-safe tool for chemical analysis, as was shown in one of the examples in this paper. As an analytical method its use is considerably expanding with the wider availability of plasma methods of mass analysis. It also provides an important tool for improving accuracy and for the study of artefacts in the determination, particularly for speciation analysis of all kind of unstable compounds.

Further study of the processes taking place in the different plasma environments will hopefully lead to more accurate analysis through a better understanding of the analytical processes, thus increasing accuracy.

In this paper, we did not go into any detail on the discussion of the preliminary part of any analysis: sampling and sample pretreatment prior to the analysis itself. These have been dealt with, up to now, in only a very limited number of books and review articles. This consistent lack of attention is surprising when one considers the overall time spent on these preparatory phases to the real analytical act and when one realises how intricately the quality of the results depends on the first and preparatory parts of any analysis. The development of clean sampling and handling techniques, which in itself involves a substantial investment of time and resources, has always been a necessary step towards obtaining, in the end, accurate and reliable analytical data. Due to their inherent sensitivity, plasma methods of analysis need to take special attention to sample pretreatment especially to avoid any contaminations.

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