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WHY ARE WE IN SEARCH OF THE METROLOGICAL BASIS OF SPECTROSCOPIC MEASUREMENTS?

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Abstract

Spectroscopic methods are widely used in analytical laboratories all over the world. Detailed knowledge about the principles of the techniques as well as knowledge of the whole analytical process are necessary to 'produce' measurement results of adequately high quality. According to the conclusions resulting from IRMM's International Measurement Program (IMEP) rounds, IMEP-3, IMEP-6 and IMEP-9 (Trace elements in water) where the participating laboratories used four different spectroscopic techniques (ETAAS, FAAS, ICP-ES and ICP-MS), that is not always the case: more than 50% of the spectroscopic results with their stated uncertainties do not overlap with the uncertainty range of the certified/assigned reference value (for ICP-MS the percentage is slightly better). It is obvious that the analytical community must put greater effort in the establishment of a better common metrological basis for (spectroscopic) measurements.

Introduction

Establishment of traceability, as defined in VIM, in results of measurements in chemistry is an essential prerequisite for comparability of results.[1] It is therefore important that analysts and end-users of the results have a clear understanding and awareness of traceability of such results.

One of the most often used families of methods are "spectroscopic methods". Hence it is worthwhile to examine more closely comparability and traceability of results obtained by these methods. That need has emerged also from observations made on results of different spectroscopic methods. In IRMM's International Measurement Evaluation Programme (IMEP), it is also interesting to examine the role of (certified) reference materials ((C)RM), since their use - or absence of use – is generally believed to make a great difference. However, results of measurements of cadmium and lead in IMEP rounds on water samples (IMEP-3, IMEP-6, IMEP-9) seem to require other than "traditional" explanations. This will be shown in this paper.

Results of measurements of cadmium and lead in water samples in the IMEP-3, IMEP-6 and IMEP-9 measurement evaluations[2]

In IMEP-3, a natural water sample and a spiked pure water sample (pure water spiked with various elements) were measured by the two reference laboratories using isotope-specific methods: isotope dilution mass spectrometry (IDMS) and neutron activation analysis (NAA), wherever possible.[3] 155 participating laboratories used their routine methods (mainly spectroscopic) to analyse and measure both samples. The spread of the results was about ±50% (Figure 1).

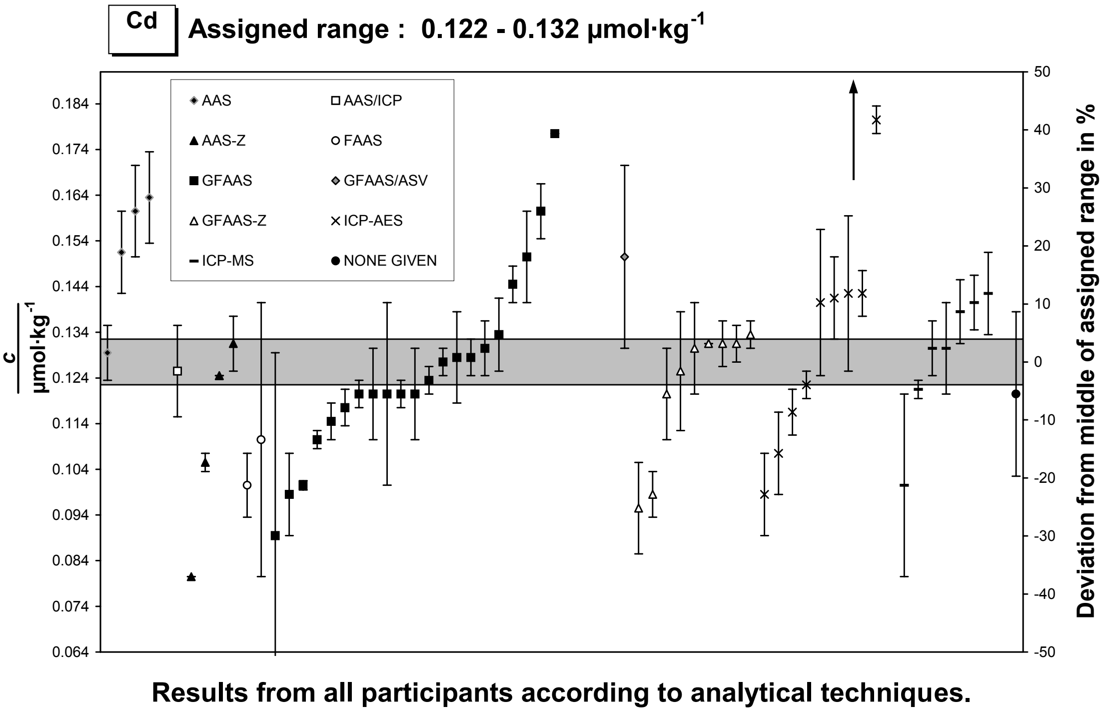

Figure 1. IMEP-3: Results of spectroscopic measurements of cadmium in natural water sample

In IMEP-6, the same type of samples was analysed by 180 laboratories in Europe.[4,5] The reference values for cadmium and lead in both samples were again established by isotope-specific methods (Isotope Dilution Thermal Ionisation Spectrometry, ID-TIMS, and Isotope Dilution Inductively Coupled Plasma Mass Spectrometry, ID-ICP-MS) by three reference laboratories. The spread of the participants' results was quite the same as in IMEP-3 (Figure 2).

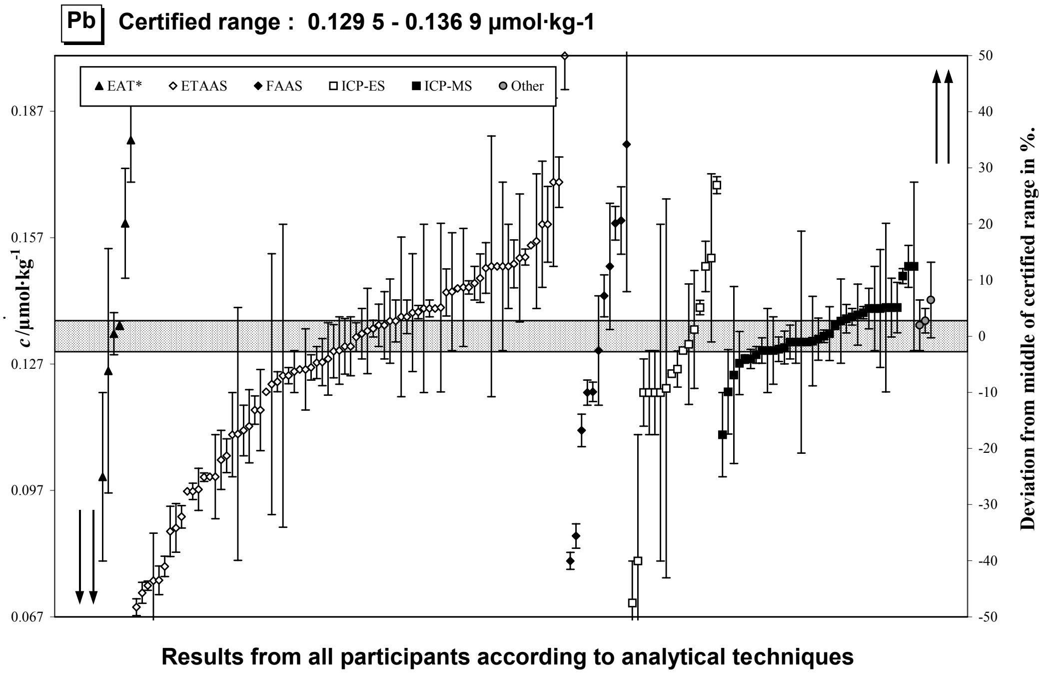

Figure 2. IMEP-6: Results of spectroscopic measurements of lead in natural water sample

In IMEP-9, a natural water sample was analysed by 201 laboratories from around the world.[6] The results (with uncertainties) of field laboratories for cadmium in the water samples of IMEP-9 are displayed in Figure 3 as measured by various spectroscopic techniques (Electrothermal Atomic Absorption Spectrometry, ETAAS, Flame Atomic Absorption Spectrometry, FAAS, Inductively Coupled Plasma Emission Spectrometry, ICP-ES, Inductively Coupled Plasma Mass Spectrometry, ICP-MS), and compared to the metrological reference values with uncertainties, obtained by IDMS used as a "Primary Method of Measurement" (PMM).[7]

The certified reference values for lead and cadmium were obtained by seven laboratories with a proven record (e.g. publications) in the use of the isotope-specific method “par excellence”: Isotope Dilution Mass Spectrometry. Measurement uncertainty evaluation of the certified reference values for cadmium and lead in the stated IMEP rounds were established applying principles defined in the ISO GUM[8].

Again the spread of the reported results was of the order of ±50%. As a rule, the majority of the results for cadmium and lead measured by ETAAS which were not within the reference range of the certified value, were below the reference range, while this varied for the other spectroscopic techniques. Quite some results were even outside ±50% of the reference range (Table 1).

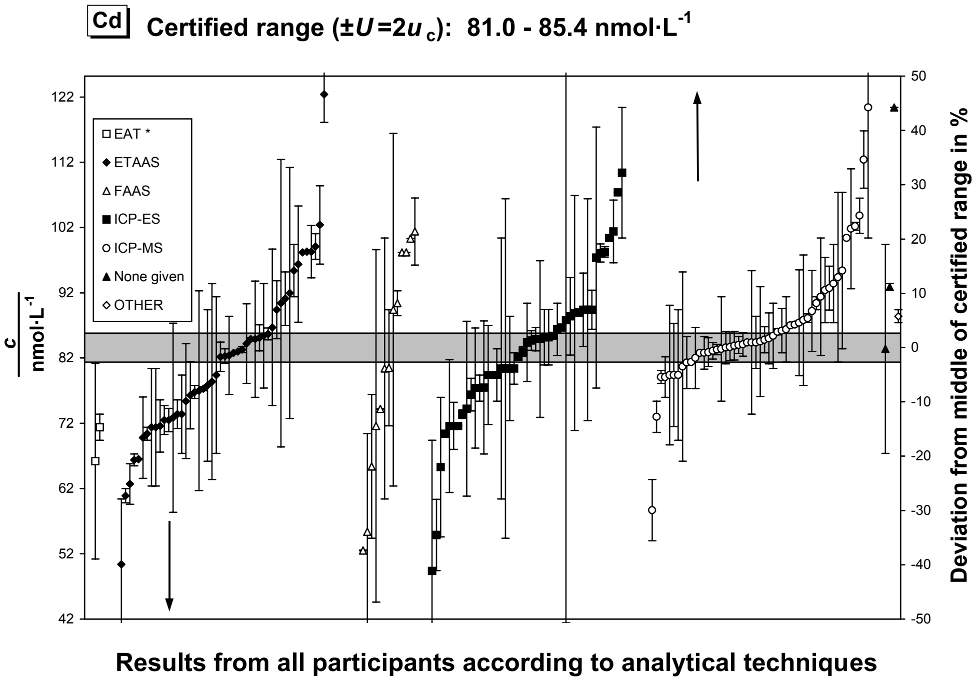

Figure 3. IMEP-9: Results of spectroscopic measurements of cadmium in water sample

Table 1. Fraction of the results (%) outside ±50% of the reference range, obtained by various spectroscopic techniques in IMEP-6 and IMEP-9

	Pb			Cd		
	IMEP-6 (NAT)	IMEP-6 (SPIKED)	IMEP-9	IMEP-6 (NAT)	IMEP-6 (SPIKED)	IMEP-9
ETAAS	9	13	10	9	9	19
FAAS	21	15	71	0	0	19
ICP-ES	24	43	25	7	8	13
ICP-MS	0	6	4	0	3	5

In Figure 4, the ratio (per laboratory) between results for natural and spiked pure water for lead measured in IMEP-6, is shown for various spectroscopic techniques. Results that are not within ±50% of the reference range of the certified value lay outside of the Figure (there were twelve such results).

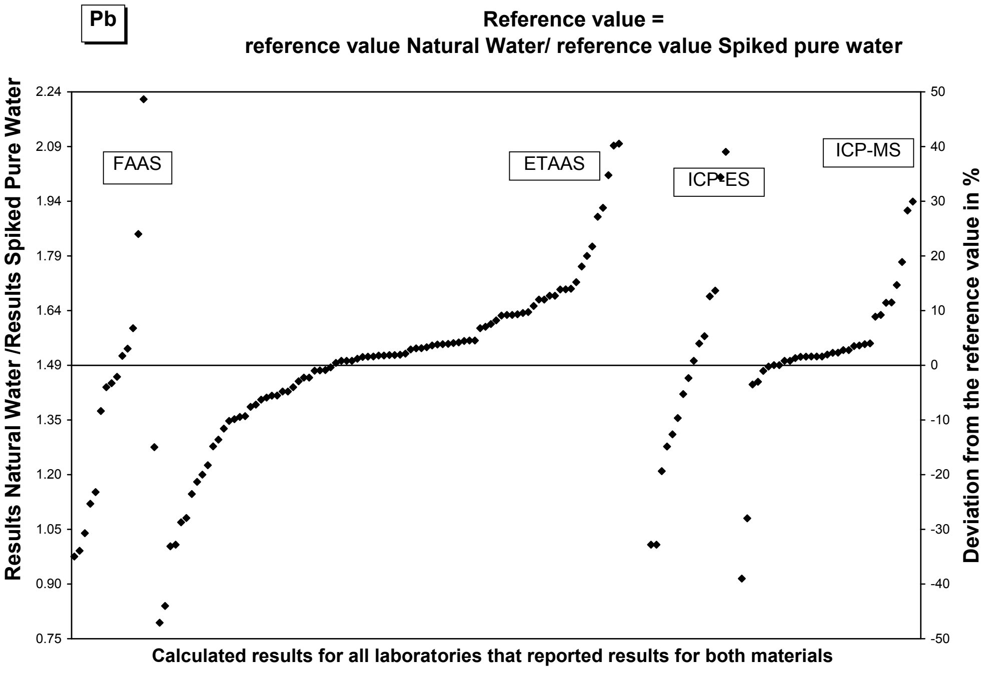

Figure 4. IMEP-6: Ratio (per laboratory) of results for lead in natural and spiked pure water samples

Discussion

As is evident from Figure 3, spread and distribution of the results obtained by various spectroscopic methods are very similar. This indicates that the way a procedure for a given method is used is a key factor in achieving reliable results, not just the method itself. The conclusion seems to be substantiated by picture of the ratios of the results for natural and spiked pure water samples shown in Figure 4, where the spiked sample in fact played the role of a reference material without the participants knowing that.

The underestimation of uncertainties is perhaps the most striking feature, visible in all Figures. The laboratories had been asked to provide an uncertainty range around their declared value “from which you claim that it contains the ‘true’ value”. Many of the stated uncertainties do not meet this requirement.

If overlapping of reference and reported ranges is taken as a criteria for satisfactory performance of the participating laboratories, the conclusions shown in Figure 5 are obtained. Again, it is evident that in general, less than half of the reported results is within the reference range.

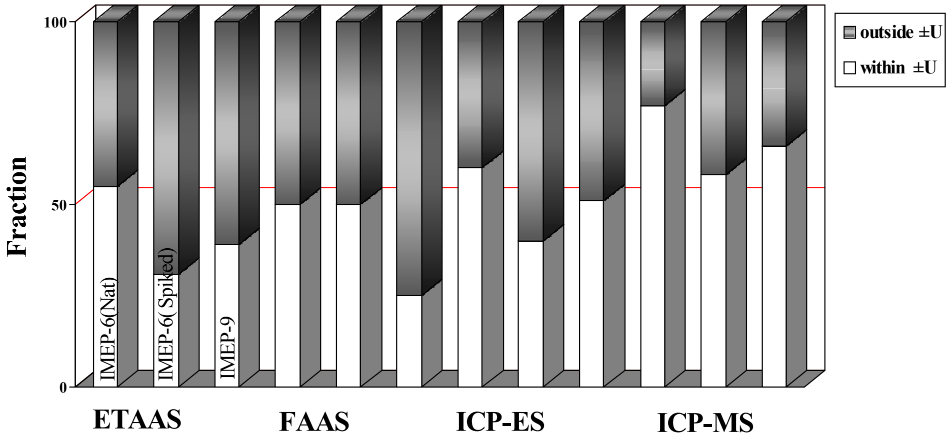

Figure 5. Cd in IMEP-6, IMEP-9: Fraction of laboratories performing satisfactorily applying various spectroscopic techniques

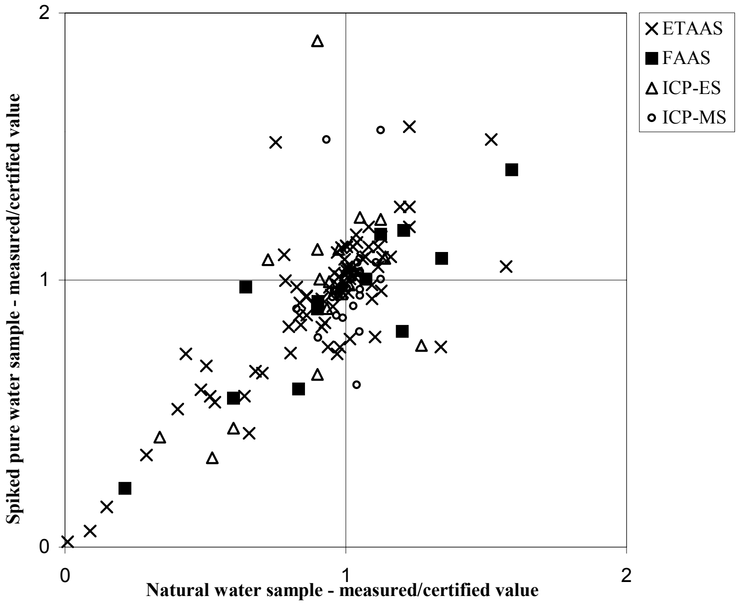

Figure 6. IMEP-6: Correlation between measured and certified values for lead in natural and spiked pure water samples

The correlation coefficients for ratios of results for lead in spiked pure water to their corresponding reference value, and same ratios of results for lead in natural water to their reference value, in the cases of ETAAS, FAAS, ICP-ES and ICP-MS, are 0.77, 0.95, 0.99 and 0.25, respectively (Figure 6). This seems to indicate that FAAS, ICP-ES and (also) ETAAS (most likely) have calibration problems, while incorrect results measured by ICP-MS are probably due to other reasons.[9]

Since the majority of incorrect results is located in the lower left quadrant ($0<x<1$, $0<y<1$), it seems that most often, sample amounts are 'lost' in some stage(s) of the analytical procedure.

Conclusions

On the basis of data, obtained during various IMEP rounds, several conclusions can be drawn.

1. The way a procedure for a given spectroscopic method is applied is very important. Using the same method, some laboratories obtain (considerably) less, some (considerably) more than the actual concentration.

2. Measurement uncertainties as declared by laboratories, are underestimated and are therefore not what they claim to be.

3. No method seems to be considerably better (or worse) than any other at the stated uncertainty level.

4. The degree of equivalence of results of any two laboratories is highly variable.

5. Whether results are fit for their intended use cannot be derived from these graphs. Certainly all laboratories are not expected to deliver results of the same quality as “reference laboratories”. In order to decide on the degree of “fitness for the intended use” of the result, it is necessary to establish a target value for uncertainty prior to the measurement in order to be able to determine, with the help of IMEP graphs (i.e. after measurement), which laboratories must (not) improve their measurement capability. So far, this has not been done by regulatory bodies.

A general conclusion is therefore that the very basic elements of “metrology in chemistry” (MiC): comparability, traceability, uncertainty and target value for uncertainty (TVU) are in bad need of clearer formulation and understanding.

References

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Povzetek

V analitskih laboratorijih se najpogosteje uporabljajo analitski postopki, ki vključujejo merjenje z različnimi spektroskopskimi tehnikami. Za ‘proizvodnjo’ rezultatov ustrezne kakovosti je potrebno podrobno poznavanje osnovnih principov merilne metode in celotnega analitskega postopka. Zaključki medlaboratorijskih preskušanj IMEP (International Measurement Evaluation Programme, IMEP) s področja analitke vod (IMEP-3, IMEP-6, IMEP-9: Sledovi elementov v vodi) kažejo, da so rezultati meritev, dobljeni z različnimi spektroskopskimi metodami, lahko zelo (pogosto tudi več kot 50 %) različni od referenčnih vrednosti, dobljenih na osnovi meritev v “referenčnih” laboratorijih s t.i. primarnimi merilnimi metodami (PMM). Ena izmed prioritetnih nalog analitikov mora biti zato izboljšanje (razumevanja) skupne meroslovne osnove za (spektroskopske) meritve.