

Concomitant Metals Analyser for Improving Productivity of an ICP-OES

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Abstract

The Concomitant Metals Analyser (CMA), provides a unique capability to analyse elements that form a hydride and also elements that do not form hydrides, using ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy). The use of a hydride forming system improves the limits of detection (LOD) by factors of $\times 5 - \times 20$ for elements: As, Bi, Se, Sb, Sn, Te, Ge and Hg. Normally hydride systems need to be used separately to the analysis for “normal” elements that do not form hydrides. The CMA improves productivity for sample matrices that include: waters, effluents, soils and cement, by doing all elements at the same time.

1 Introduction

The ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) is a multi-element technique which allows the analysis of 75 elements in the Periodic table. ICP-OES is particularly suitable for the determination of traces up to major elements presented in liquid form. To achieve this, many samples that are solid or viscous liquids e.g. metals, rocks, plastics, oil etc. ^{[1], [2]}, are usually dissolved in a solvent, whether acid, a fusion or an organic solvent, prior to introduction to the ICP spectrometer.

The Concomitant Metals Analyser (CMA) was invented and patented ^[3] by JY in Longjumeau, France. In ICP-OES, the conventional nebulizer has typically a 2 % efficiency to create droplet sizes of less than 4 microns, this is thought to be desirable for best sensitivity and minimal interferences. Hydride systems ^{[4] - [6]} are used to enhance the detection of some historically important and yet difficult elements. The CMA system uses sodium borohydride that reacts with hydrochloric acid to form nascent hydrogen radicals. These hydrogen radicals react with the some elements (As, Bi, Se, Sb, Sn, Te, Ge) to form the volatile hydrides ^[7] (Hg is reduced to the elemental state).

The 98 % of sample waste created is retained in a small cavity, this is then mixed with sodium borohydride and hydrochloric acid that is introduced into that same cavity. Volatile hydrides are then formed and these are swept up into the torch injector to the plasma (Fig. 1).

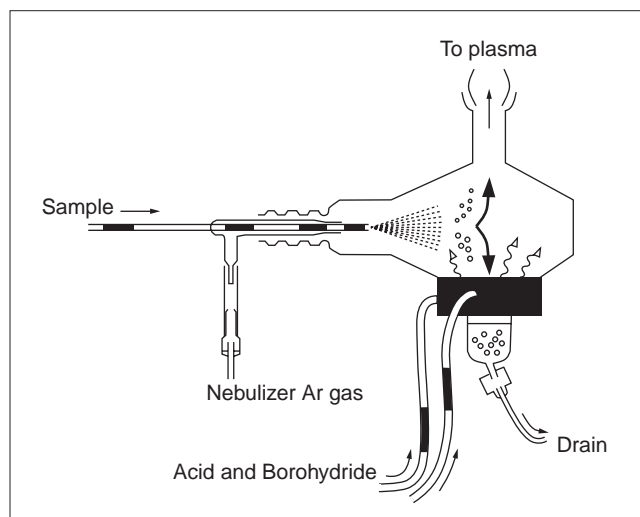


Fig. 1 CMA Nebulizer

In this manner, little difference for detection limits are seen compared with the conventional nebulization system for the “normal” elements, while the hydride elements are enhanced by between $\times 5$ and $\times 20$ depending on the element.

The resultant total analysis for all elements helps with the laboratory productivity. Productivity is becoming an ever increasing priority to lower analysis costs and therefore prices to customers, especially in environmental and contract labs.

In this study ^[8] different matrices were tried with changing parameters (Table 1) to identify the capabilities and also to identify what are important.

Table 1 Elements Investigated and Their Wavelength

Wavelengths used	
As	189.042 nm
Sb	206.833 nm
Se	196.090 nm
Hg	194.227 nm

2 Effect of Hydrochloric Acid Concentration

This was investigated for the following suite of elements As, Se, Sb, Hg; the results are shown in Fig. 2. It can be seen that low acidity gives high As and Sb signals, in contrast, the Se signal becomes lower, while Hg is unaffected by acid concentration. Due to this disparity of optimal conditions it is recommended that if Se and other hydride elements are required at the same time, then one should keep the acid concentration the same for both samples and standards and decide which element is most important.

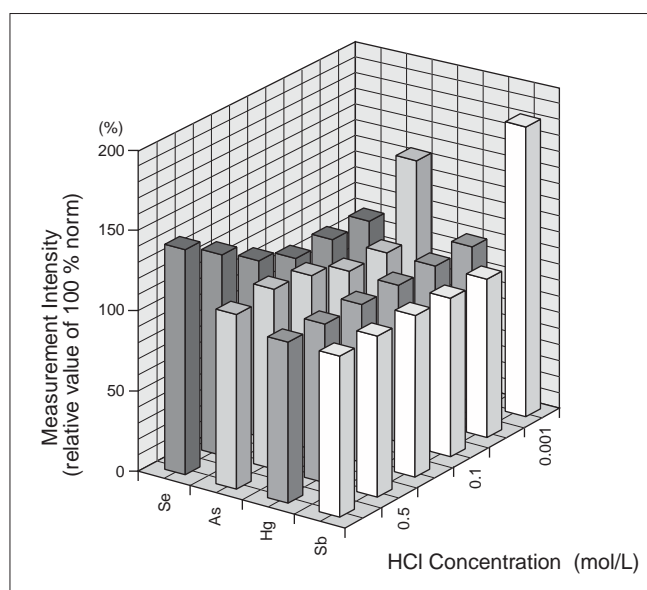


Fig. 2 Effect of HCl Concentration on Measured Intensity of As, Se, Sb, and Hg

3 Effect of Oxidation State

The oxidation state effects were investigated to see what signal changes would be found on the various elements. Oxidation state had no effect on the Hg signal as the form required for enhanced performance, is elemental Hg. However, there was a dramatic effect of signal change with oxidation state for Se, whereby there was no response from Se⁶⁺ or Se²⁺. This makes it absolutely essential to

have Se only in the Se⁴⁺ form and poses further chemistry problems for routine analysis. To ensure this, all samples requiring Se determination must be pre-treated by gentle warming with a high concentration of HCl e.g. concentrated or 5 mol/L HCl, prior to ICP analysis. The effects on As (Fig. 3) and Se were seen to be significant enough to need to maintain the same oxidation state for all samples and standards (Table 2).

It should be noted that although Pb does form a hydride, the conditions are diametrically opposite to any other hydride forming element and therefore one must use oxidising conditions, created by use of concentrated hydrogen peroxide (H₂O₂).

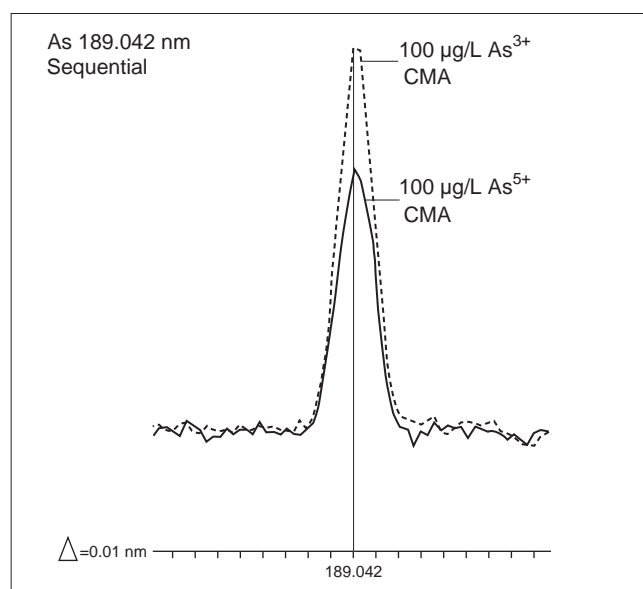


Fig. 3 As Oxidation State Effect

Table 2 As and Sb Oxidation State Effects of 1 % NaBH₄

	Net int 100 µg/L	Bkg int µg/L	BEC µg/L	LOD µg/L	LOD (rock 5 g/L)	Factor: CMA / conventional
As ³⁺	460	175	38.0	0.76	0.15	12
As ⁵⁺	330	175	53.0	1.06	0.21	8
Sb ³⁺	1200	451	37.6	0.75	0.15	20
Sb ⁵⁺	450	451	100.0	2.00	0.40	8
Se ⁴⁺	310	259	83.0	1.66	0.33	10
Hg (194 nm)	1000	104	10.4	0.20	0.04	16

BEC : Background Equivalent Concentration

LOD : Limit of Detection

4 BH₄ Effects

As can be seen in Fig. 4, it was found that higher BH₄ concentrations gave generally better signal except for Sb³⁺. Higher BH₄ concentrations also gave better correlation for different oxidation states (Fig. 5) by improving the oxidation state ratios close to 1. However, precision expressed as % RSD got worse with more than 1 % NaBH₄ solution (Fig. 6).

Moreover, there were increased transition element effects. Transition elements present in the matrix could have an effect on final signal^{[9]–[12]}. An example is seen with the determination of Se in the presence of Cu^{[13], [14]}. With only small concentrations of Cu, no hydride is formed because the Se reacts with the Cu to form CuSe

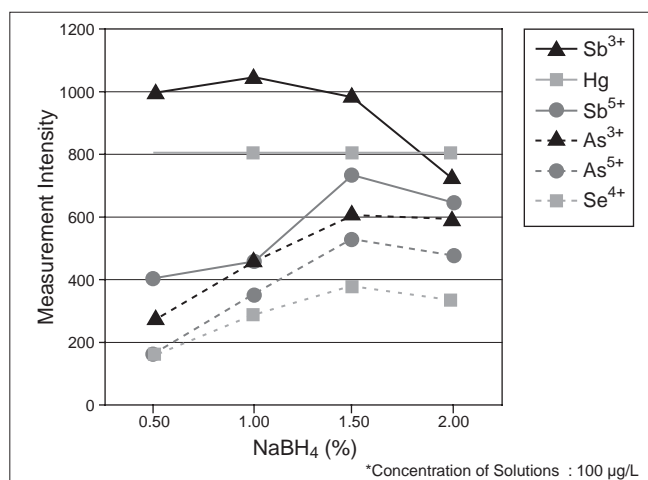


Fig. 4 Effect of the Borohydride Concentration on the Intensity of the Species

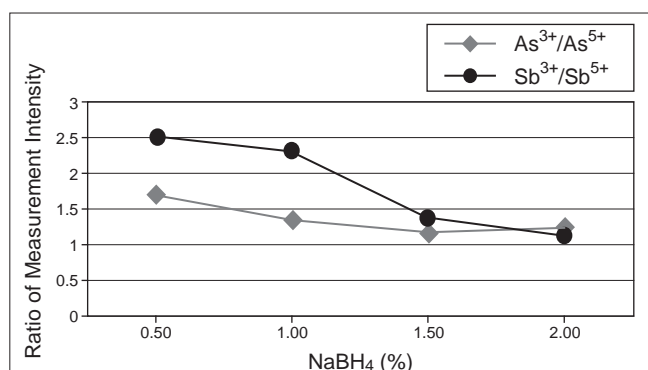


Fig. 5 Effect of the Borohydride Concentration on the Ratio of Different Oxidation States of As and Sb

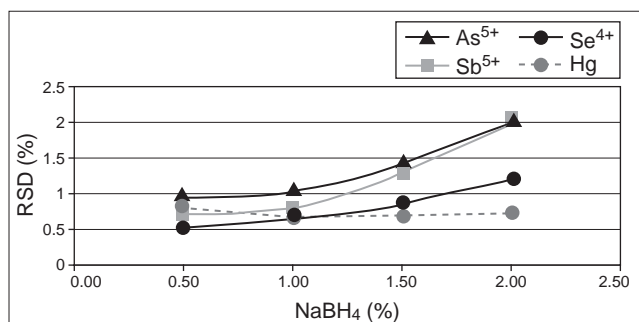


Fig. 6 Effect of Borohydride Concentration on the RSD (Relative Standard Deviation) of the Species

To avoid the strong reduction involving KI pre-treatment after Aqua Regia (3:1 ratio HCl:HNO₃) dissolution for certain sample types e.g. soils, rocks, it was found important to use 5+ oxidation state for both As and Sb for calibration standards. No KI reduction requires As⁵⁺ and Sb⁵⁺ for calibration in a 1 % BH₄ solution, however, it is necessary to use As³⁺ for the calibration standard for a KI reduction.

For the reason as previously mentioned, Se is not possible if KI reduction used, because this would push the oxidation state too far to the +2 state. The use of a stronger 1.7 % BH₄ solution was found to minimise the effect of oxidation state differences, with the oxidation state ratio trending to ~1, i.e. no effect of oxidation state for the analysis.

A large Hungarian survey was carried out called Békés county survey and to test the accuracy of the As analysis, a comparison of sample results was made by comparing ICP-OES + CMA with AAS (Atomic Absorption Spectrophotometry) + hydride generator. The results (Fig. 7) show excellent correlation of the As results with classical hydride generation on an AAS.

No KI was added in this particular work because the samples had been stored for over 6 months and during that time, the oxidation state had changed completely to As⁵⁺. However, for fresh samples KI would need to be added for both samples and calibration standards (As³⁺ for calibration), also a higher Na BH₄ would need to be used, to minimise oxidation state effects described earlier.

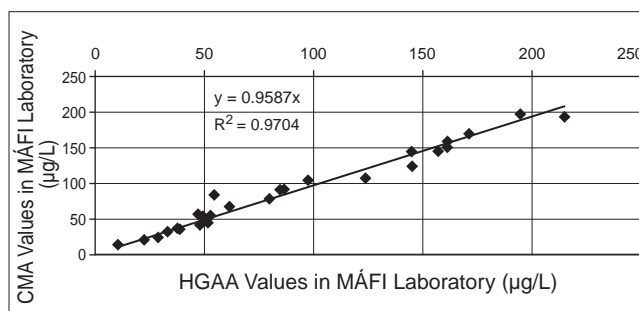


Fig. 7 Comparison of Békés County Survey of Arsenic Waters by HGAA and CMA Methods

5 CMA Analysis of Digested Solid Samples

Aqua Regia digestion always ensures the higher oxidation state is achieved and this is ideal for As^{5+} , Sb^{5+} . However, Se needs boiling with 5 mol/L or concentrated HCl to convert the Se^{6+} to the required Se^{4+} . It should be noted that, there has not been found to be any effects of any parameter for Hg determinations. It was also found that from this survey that there were no effects from the various transition elements present in the various CEN[®] CRM's. Fig. 8 shows As analysis and Fig. 9 shows Se analysis.

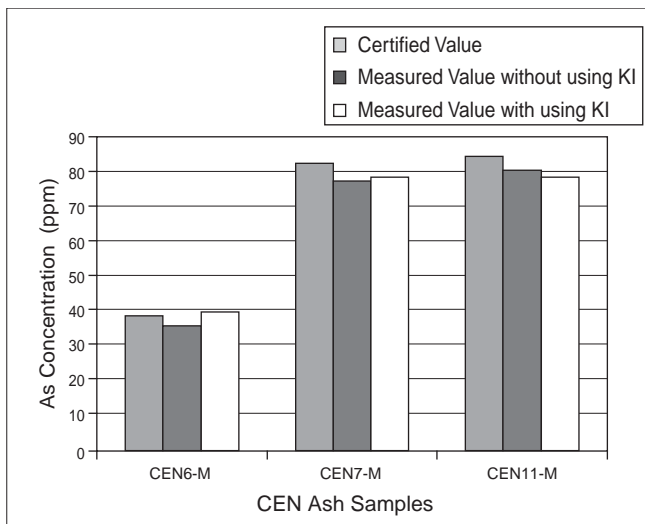


Fig. 8 Arsenic Analysis of CEN Ash Samples by Aqua Regia Digestion

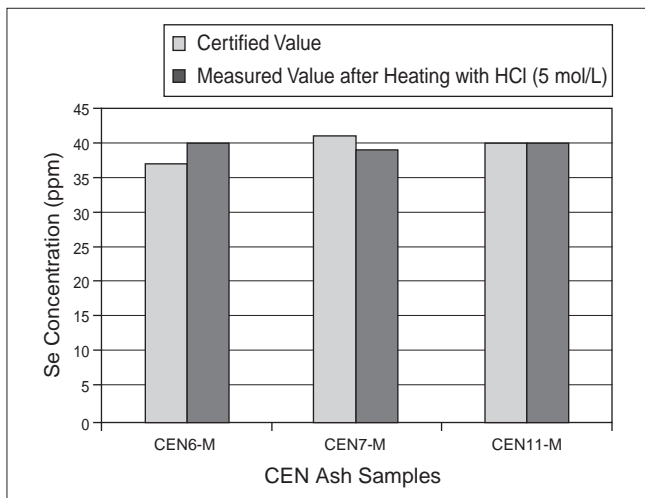


Fig. 9 Selenium Analysis of CEN Ash Samples by Aqua Regia Digestion

As part of the FOREGS (Forum of European Geological Surveys) programme, a portion of 3,000 samples in the FOREGS project in Hungary were analysed by CMA using a JY ICP-OES. The samples were a variety of river sediments, soils and ash. The analysis was compared with an Altec AMA-254 solid sampling technique with the same samples analysed by CMA digested in Aqua Regia. Fig. 10 and 11 show excellent correlation of results obtained.

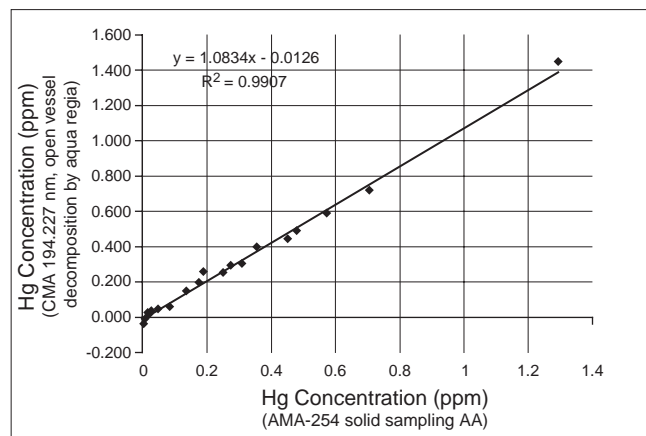


Fig. 10 Correlation of Mercury Measurement of FOREGS Samples between Aqua Regia Digestion CMA and AMA-254 Solid Sampling Atomic Absorption Photometry

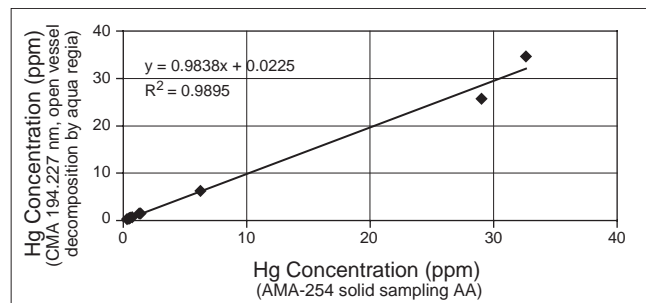


Fig. 11 Correlation of Mercury Measurement in Soil and Ash between Aqua Regia Digestion CMA and AMA-254 Solid Sample Atomic Absorption Photometry

Grating & OEM

Emission

Raman

Fluorescence

Thin Film

Optical Spectroscopy

Forensic

6 CMA – Certified Cement Samples

A set of “Round Robin test” samples were analysed with a thorough acid digestion involving HF, HClO₄, HCl, and HNO₃ acids and H₂O₂ to give a final cement solution concentration of 5 g/L. The sample stock solutions were then split into two; this enabled a further pre-treatment on the samples for Se and the other hydride elements.

Work described earlier had identified the need to make a gentle reduction for Se. Gentle heating for 10 minutes using concentrated HCl was used and a final dilution of 1:1 made for Se determination. A stronger reduction was required for the other hydride elements involving a mixture of 7.5 % (w/v) KI & 7.5 % (w/v) ascorbic acid.

Both semi-quant and standard quantitative analysis were made using the standard additions method for the determination of 18 elements in the cement samples. The hydride results are shown in Table 3 and 4.

Table 3 Cement “Round Robin” Sample Analysis Result 1

HNO ₃ 0.5%				
Element	Wavelength (nm)	BEC (mg/L)	RSD (%)	LOD (µg/L)
Hg	184.890	0.0028	0.72	0.0605
Hg	194.163	0.00406	0.81	0.0987
As	189.042	0.0125	0.78	0.293
Sb	217.581	0.0206	0.50	0.309
Se	196.026	0.0343	0.51	0.525
Sn	189.989	0.0176	0.75	0.396
Te	214.281	0.198	0.52	3.09
Te OPT*	214.281			

HNO ₃ 1% - HCl 1% + Ca 1g /L				
Element	Wavelength (nm)	BEC (mg/L)	RSD (%)	LOD (µg/L)
Hg	184.890	0.00321	0.93	0.0896
Hg	194.163	0.00418	0.91	0.114
As	189.042	0.0134	0.65	0.261
Sb	217.581	0.0205	0.44	0.271
Se	196.026	0.0344	0.63	0.650
Sn	189.989	0.0186	0.64	0.357
Te	214.281	0.196	0.43	2.53
Te OPT*	214.281	0.059	0.55	0.974

* Optimised just for Te

Table 4 Cement “Round Robin” Sample Analysis Result 2

Samples	1		2		3		4	
	Conc. Obtained (ppm)	Conc. Certified (ppm)	Conc. Obtained (ppm)	Conc. Certified (ppm)	Conc. Obtained (ppm)	Conc. Certified (ppm)	Conc. Obtained (ppm)	Conc. Certified (ppm)
As	14.9±0.4	15.3±1.5	4.7±0.3	5.4±0.3				
Sb	5.2±0.3	5.6±0.3						
Se	4.6±0.3	4.6±0.9						
Sn					5.7±0.2	7.6±3		
Te							0.5±0.06	0.5*

Confidence level is 3 * SD

* Not fully certified

7 Conclusion

ICP-OES with CMA has been found suitable for use on a wide variety of environmental samples including: potable waters, rivers, waste waters, sewage as well as soils, ash, river sediments and cement. Little or no effect was found from transition elements potentially present in these samples. Some oxidation state pre-treatment is required for some samples and NaBH₄ concentration should be kept constant for all samples and standards.

The fact that hydride forming elements can be determined at the same time as “normal” elements by using the CMA, can result in improved laboratory productivity in a real situation, thus reducing the cost of analysis.

Acknowledgments are given to the Hungarian Institute for Geology for permission to use their results.

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