



Comparison of Classical Hydride Generator and Concomitant Metals Analyzer (CMA)

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1 Introduction

To improve detection limits for elements such as Hg, As, Sb, Se and Sn, one can use hydride generation. This is particularly useful for environmental analysis, where the concentration ranges are close to the $\mu\text{g/L}$ level. One of the main drawbacks of this technique, until recently, has been the requirement of performing the analysis twice: once for the normal elements and the other for the hydride species. Additionally, it was necessary to replace the standard spray chamber system with a hydride generator device. With the CMA, it is not necessary to change anything. Using the same conditions and cassette, all the normal elements and hydride species can be determined in one analysis run and the detection limits are improved by a factor of 5 to 50 for the hydride forming elements.

2 Principle

2.1 Technique used

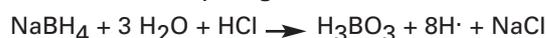
The elemental analysis of solutions was undertaken by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The sample is nebulized then transferred to an argon plasma. It is decomposed, atomized and ionized whereby the atoms and ions are excited. We measure the intensity of the light emitted when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths and these lines can be used for quantitative analysis after a calibration.

2.2 Description of the hydride generation process

This method involves forming hydrides of elements such as As, Sn, Se, Sb plus Hg as the free metal vapor. Being volatile, they can more easily be carried by the argon into the plasma. The

method is also applicable to Bi, Ge, Te and Pb. The hydride generator is based on the reaction of sodium borohydride, hydrochloric acid and the sample.

Formation of hydrogen free radical:



Formation of the volatile metal hydride (gas)



where E is the hydride-forming element of interest, such as As, Se, Te, etc... and m may or may not be equal to n. This formation of a metal hydride is a continuous reaction not a batch process. Hg^{2+} is reduced to Hg^0 and, as the Hg vapor is also volatile at room temperature, it is easily transported to the plasma.

3 Conventional hydride generation

The HORIBA Scientific conventional hydride generation system is shown in Figure 1. The sodium borohydride and the sample are mixed with acid, controlled by separate peristaltic pumps, in a polypropylene "T" tube reaction chamber. The liquid and gas phases are then rapidly transformed through a short Teflon tube to a gas/liquid separator.

The gaseous products (hydrides and hydrogen) are flushed from the gas/liquid separator by a controlled stream of argon carrier gas, the flow rate of which is set by the flow meter of the nebulization circuit from the gas control panel of the ICP.

As the reaction liquids are pumped into the separator and the carrier gas purges the products into the ICP torch, a pressure differential occurs in the two arms of the U-tube. Excess liquid is transferred to waste via the U-tube drain.

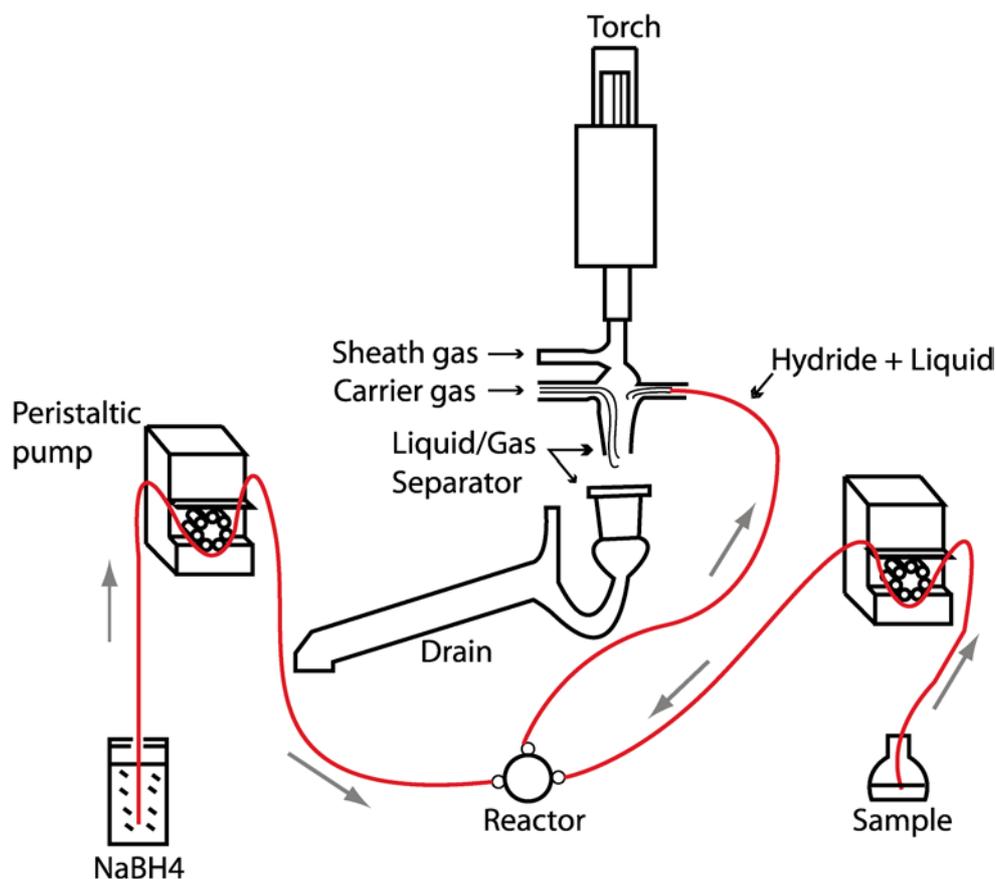


Figure 1: Hydride Generator

4 Concomitant Metals Analyzer (CMA)

The sodium borohydride and the acid solution are pumped by the peristaltic pumps and mixed in the spray chamber. The sample is nebulized and the reaction takes place in the spray chamber.

The gaseous products, hydrogen, the hydrides and the aerosol, are carried by the argon to torch while the excess liquid is evacuated through the drain. (See Figure 2). The CMA is a patented device available only from HORIBA Scientific.

4.1 Reagent and sample preparation

4.1.1 Sodium borohydride solution

Solid NaBH_4 was dissolved in a solution of NaOH 0.5 M to obtain a final solution of about 1% by weight and then filtered. Under these conditions, the solution will be stable, if kept far from any heat source and in a cool environment, for two days.

Warning: if the NaBH_4 solution is stored in a plastic bottle check that its cover is not too tightly sealed as the solution will slowly decompose and produce hydrogen, which could cause the bottle to explode. The reagents used are corrosive and potentially flammable so all standard precautions should be taken when handling these products.

4.1.2 Acid solution



The optimum acid concentration for most elements is in the range of 1 to 6 M. HCl is the best acid. Other acids such as HNO_3 (2M) can be used, but H_2SO_4 and HClO_4 must be avoided due to their strong oxidizing properties.

4.1.3 Sample solutions

The sample solutions should not contain particles that might obstruct the pump capillaries therefore, it is recommended that solutions should be filtered.

4.1.4 Pb analysis

If Pb is required to be analyzed at lower concentrations, H_2O_2 is required to create special conditions for the formation of PbH_4 .

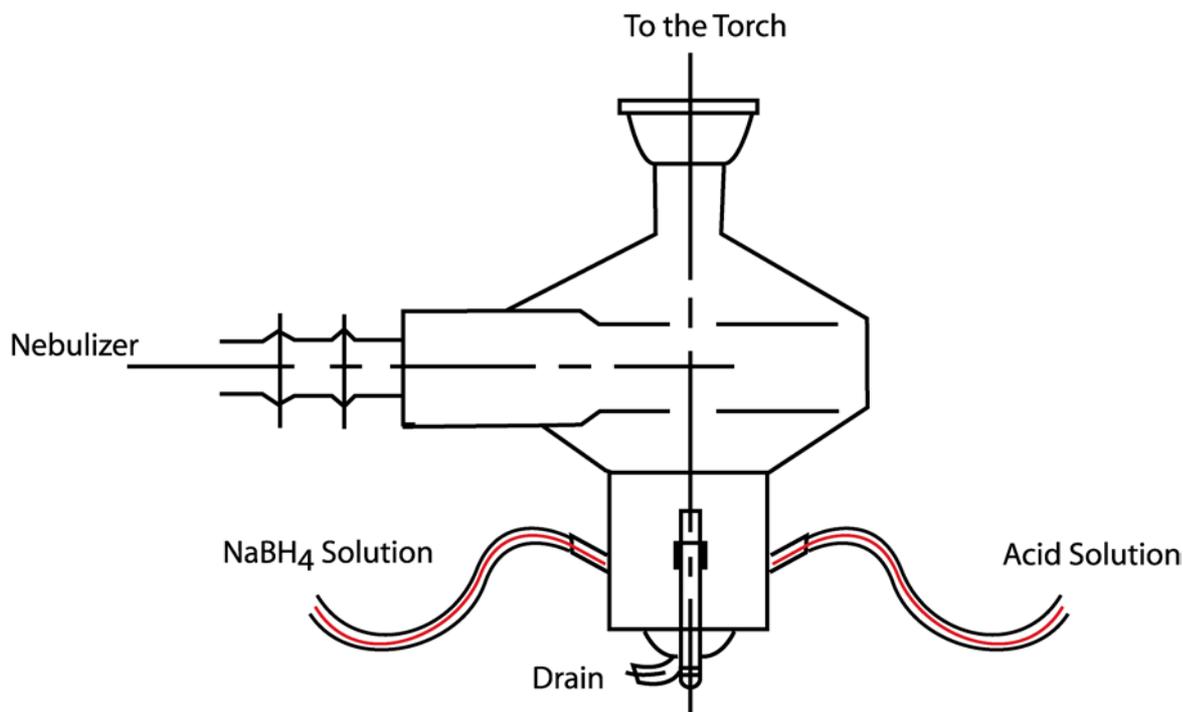


Figure 2: Concomitant Metals Analyzer (CMA)



5 Results

The measurements were made on a PANORAMA with axial plasma. The improvement factors are valid for all HORIBA Scientific instruments, because it depends on sample introduction only. Hydride improvement factors depend on the conditions used.

Table 1: Limits of Detection

Element	LOD Without CMA ($\mu\text{g/L}$)	LOD With CMA ($\mu\text{g/L}$)	Improvement factor found
As	3.1	0.4	8
Be	0.10	0.10	
Ca	0.69	0.91	
Cd	0.28	0.29	
Co	0.38	0.36	
Cr	0.51	0.50	
Cu	0.35	0.34	
Fe	0.13	0.12	
Hg	3.2	0.036	90
Mn	0.06	0.10	
Ni	0.42	0.52	
P	3.1	1.9	
Pb	1.9	2.5	
Sb	2.2	0.31	7
Se	4.0	0.30	13
Sn	1.7	0.072	24
Tl	1.8	2.1	
Zn	0.21	0.17	

6 Summary

The CMA provides enhanced productivity whereby all elements can be analyzed in one run, fulfilling all environmental detection limit requirements of the US-EPA. The CMA can be fitted to any model in the Jobin Yvon ICP product range very easily, allowing rapid and efficient analysis of hydride forming elements down to ultra trace levels. The CMA is very simple to set up and can be used as the standard sample introduction system. If a run does not require the use of hydride generation to reach ultra-trace levels, simply turn off the pump that transports the hydride generation reagents to the chamber.

The use of the CMA hydride generation system provides increase sample throughput and sensitivity for difficult elements, with sub-ppb detection limits being routine.

Table 2: Comparison of CMA and classical hydride

	Classical hydride generation	CMA
Elements that can be determined in a single run	Hydride forming elements	All elements
Sample preparation	Acidification needed to obtain similar concentration for all solutions	None

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