AN APPLICATION REPORT FROM
SPECTRO ANALYTICAL INSTRUMENTS

ICP-133 Rev. 1



SPECTRO**GREEN**

Analysis of Trace Elements in Water Using Axial Plasma Observation and a Combined Pneumatic-Hydride Generating Sample Introduction

Introduction

A convenient way to improve the sensitivity for elements such as As, Sn, Se and Sb is available via the generation of their gaseous hydrides, usually formed by the reaction of an acidified sample solution with sodium borohydride. This permits the ICP-OES to conduct analyses at sub ppb levels, a concentration range otherwise confined to ICP-MS. With the Hydramist [1] a all-in-one system was tested now.

The system allows the simultaneous sample introduction using hydride generation as well as normal pneumatic nebulization and thus offers a simple, fast, precise, accurate and very cost-efficient method for the analysis of trace elements. Unlike other separate hydride systems, it does away with requiring the change of the sample introduction system and a second measurement and still provides the improved sensitivity for the hydride generating elements, while maintaining the sensitivity for the others.



Instrumentation

All measurements were performed with the SPECTROGREEN ICP optical emission spectrometer (SPECTRO Analytical Instruments, Kleve, Germany) with twin interface plasma observation, which enables the automatic axial and radial observation of the plasma with every measurement. The SPECTROGREEN features a Paschen-Runge spectrometer mount, employing the proprietary Optimized Rowland Circle Alignment (ORCA) technique. Consisting of two hollow section cast shells, optimized small volume and 15 linear CMOS detectors, the wavelength range between 165 and 770 nm can be analyzed, allowing complete spectrum capture within 4 s. Due to the unique reprocessing capabilities of the system, a new measurement is not required even if additional elements or lines are to be determined at a later point in time. The optic is hermetically sealed and filled with argon, continuously circulated through a filter, which absorbs oxygen, water vapor and other species. High optical transmission in the UV is achieved, allowing the determination of non-metals as well as the use of prominent and interference free lines in this region.

Plasma power	1250 W
Observation mode	Axial
Coolant flow	13.0 L/min
Auxiliary flow	0.8 L/min
Nebulizer flow	0.8 L/min
Plasma torch	Quartz, 1.2 mm Injector tube
Spray chamber	Hydramist
Nebulizer	Seaspray
Replicate read time	50 sec.

Table 1 : Typical ICP-OES operating conditions

An air-cooled, 27.12 MHz, free running type LDMOS ICP-generator is installed, which ensures excellent stability of the forward power even in the case of rapidly changing sample loads. All relevant ICP operating parameters are software controlled, allowing easy selection of the optimum operating conditions. For sample introduction, a Seaspray nebulizer and a Hydramist [1] spray chamber was used. The ICP operating conditions are given in Table 1.

Hydramist

As sample introduction system a Hydramist chamber in combination with a Seaspray nebulizer was used. With this, sample introduction using pneumatic nebulization and hydride generation is possible. All solutions were acidified with 3.2% (w/w) HCl [2].

The operating conditions are given in Table 2.

The Hydramist sample introduction system is shown in Figure 1.

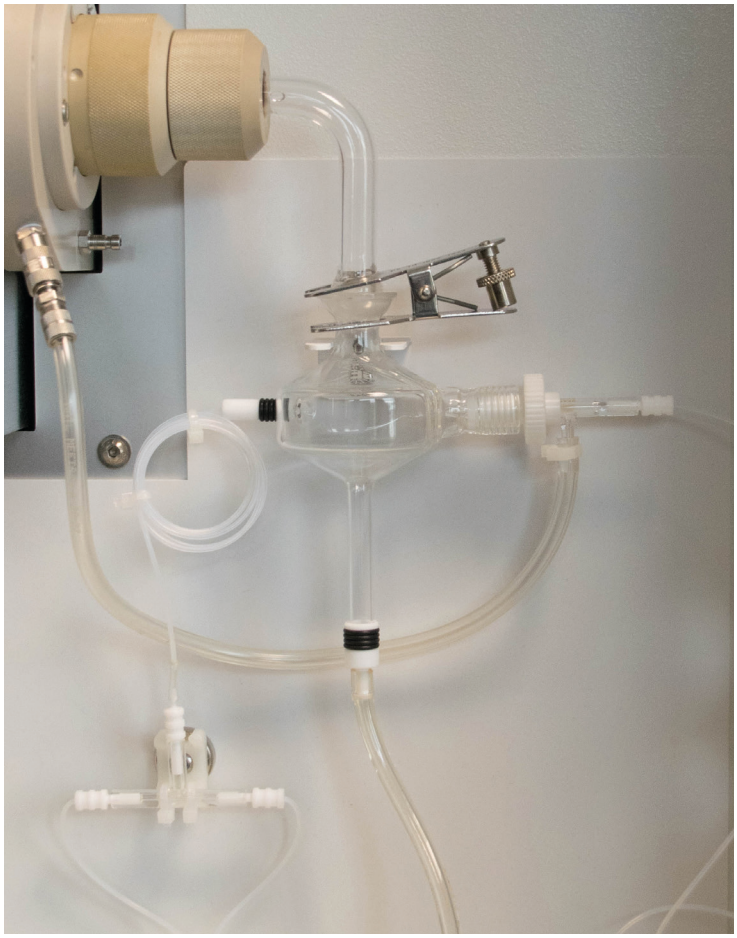


Figure 1: Hydramist sample introduction system

Concentration hydride generation reagent	10g/L NaBH4 [2] + 4g/L NaOH [3]
Hydride sample aspiration rate	2.6 mL/min
Reagent aspiration rate	2.6 mL/min
Sample/reagent pump tube	white - white
Pneumatic sample aspiration rate	1.4 mL/min
Pneumatic sample pump tube	black - black

Table 2: Sample introduction operating conditions

Calibration

A commercially available multi-element standard [5], was used to prepare the standards. The analyte concentrations of the calibration standards are listed in Table 3.

Element	Std.1 [µg/L]	Std.2 [µg/L]	Std.3 [µg/L]	Std.4 [µg/L]	Std.5 [µg/L]
Ag	0	0.5	1	2	2.5
Al, As, Ba, Be,Cd, Co, Cr, Cu, Fe, Hg, Li, Mn,Mo, Ni, Pb, Sb, Se, Si, Sn, Sr, Tl, V, Zn	0	2	4	8	10
K, P	0	10	20	40	50

Table 3: Calibration standards

Element	λ [nm]	LOD (3σ) [µg/L]
Ag	328.068	0.5
Al	167.078	0.03
As	189.042	0.2/0.8*
Ba	455.404	0.05
Be	313.042	0.06
Cd	214.438	0.06
Co	238.892	0.3
Cr	205.618	0.2
Cu	324.754	0.6
Fe	238.204	0.2
Hg	184.950	0.01/0.4*
Mn	257.611	0.04
Ni	231.604	0.4
P	177.495	1.0
Pb	220.353	1.2
Sb	206.833	0.2/0.9*
Se	196.090	0.08/1.0*
Sn	189.991	0.02/0.3*
Tl	190.864	0.8
V	292.464	0.9
Zn	213.856	0.09

Table 4: Typical Limits of Detection (LOD)

**LOD = 3 RSD$_b$ c/100*SBR*

**LOD using normal pneumatic nebulization*

Results and Discussion

Table 4 shows the selected wavelengths and the limits of detection (LOD) achieved. The LODs were calculated according to the equation [6]:

LOD = 3 RSD$_b$ c/100*SBR

Where:

RSD$_b$ – relative standard deviation of 10 replicates of the blank [%]

c – concentration of the standard

SBR – signal to background ratio

Accuracy

The accuracy of this method was investigated by the analysis of a spiked tap water sample and NIST reference material 1643f [7].

Table 5 shows the concentrations of the prepared spike with the measured concentrations and the recovery in percent. Good values were achieved for all elements.

Element	Spike conc. [µg/L]	Measured conc. [µg/L]	Recovery [%]
Ag	1.25	1.44	115.2
Al	5	5.26	105.2
As	5	5.01	100.2
Ba	5	4.80	96.0
Be	5	5.03	100.6
Cd	5	4.81	96.2
Co	5	4.86	97.2
Cr	5	5.21	104.2
Cu	5	5.10	102.0
Fe	5	4.70	94.0
Hg	5	4.91	98.2
Mn	5	4.88	97.6
Ni	5	4.94	98.8
P	25	25.00	100.0
Pb	5	4.70	94.0
Sb	5	4.78	95.6
Sn	5	4.59	91.8
Tl	5	4.71	94.2
V	5	5.18	103.6
Zn	5	5.10	102.0

Table 5: Spike Recovery

Table 6 shows the certified concentrations of the NIST Reference material 1643f, the measured concentrations and the recovery in percent. Also here the measured concentrations are in good agreement with the given values.

Element	NIST 1643f [µg/L]	Measured Conc. [µg/L]	Recovery [%]
Al	133.8	125	93.4
As	57.42	57	99.3
Ba	518.2	482	93.0
Be	13.53	12.9	95.3
Cd	5.89	5.76	97.8
Co	25.3	23.5	92.9
Cr	18.5	17.5	94.6
Cu	21.66	22.5	103.9
Fe	93.44	91.1	97.5

Element	NIST 1643f [µg/L]	Measured Conc. [µg/L]	Recovery [%]
Mn	37.14	34.9	94.0
Ni	59.8	52.2	87.3
Pb	18.488	17.9	96.8
Sb	55.49	49.8	89.7
Se	11.7	11.5	98.3
Tl	6.892	6.78	98.4
V	36.07	33.6	93.2
Zn	74.4	69.3	93.1

Table 6: NIST 1643f

Conclusion

The SPECTROGREEN TI utilizing axial plasma observation mode for the measurement, combined with a Hydramist sample introduction system, allows the simultaneous sample introduction using hydride generation as well as normal pneumatic nebulization. This offers a simple, very fast, precise and accurate, and thus a very cost-efficient method for the analysis of trace elements in water. Unlike other separate hydride systems, it does not require the change of the sample introduction system and a second measurement while still providing the improved sensitivity for the hydride forming elements, maintaining the sensitivity for the other elements. Excellent precision and recoveries were determined for a spiked sample as well as a certified reference material. In conjunction with an autosampler, the instrument can be fully automated. Independent from the number of lines and elements, an analysis (including three replicates and pre-flush) can be performed in less than three minutes.



References

[1] Glass Expansion, Australia
[2] Hydrochloric acid 32% suprapur™, Merck GmbH, Germany
[3] Sodium Boron Hydride suprapur™, Merck GmbH, Germany
[4] Sodiumhydroxide p.a.™, Merck GmbH, Germany
[5] Multi Element Standard EPA Lpc, 20 mg/L, Bernd Kraft GmbH, Germany
[6] P. W. J. M. Boumans, Spectrochim. Acta 46B, 431 (1991)
[7] NIST 1643f, NIST, U.S. Department of Commerce

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