

Challenge

Trace determination of As, Sb, Se, Hg, Pb, Cd in surface and drinking water.

Solution

Reliable routine analysis with lowest detection limits using AAS in combination with the hydride and HydrEA technique.

Trace Analysis of Toxic Elements in Surface and Drinking Water by Combined AAS Techniques

Introduction

Safe drinking water is essential for health. Even low concentrations of toxic elements can be harmful if contaminated water is consumed regularly over a long period of time. Many groundwater sources supplying public and private wells contain a high concentrations of naturally occurring arsenic. Lead contamination can be caused, for example, by slow dissolution of lead water pipes. In addition, groundwater and surface water can be contaminated with toxic elements through environmental pollution. Therefore, strict regulations apply to the control of drinking water, such as the Drinking Water Directive of the European Commission^[1], the U.S. EPA National Primary Drinking Water Regulations (NPDWR)^[2], or the German Drinking Water Regulation (TrinkwV)^[3].

The limits for the most toxic elements are usually regulated from 1 to 10 µg/L. Atomic absorption spectroscopy with graphite furnace and hydride technology meets the high requirements of drinking water analysis, such as lowest detection limits and high accuracy. It is simple, robust, and suitable for routine use by means of automation. The hydride system HS60 with flow injection allows an automated sample processing with detection limits down to 0.05 µg/L for the hydride forming elements. With the integrated gold-collector, mercury can be enriched and measured down to 0.02 µg/L. For even greater sensitivity, the so-called HydrEA technique can be used. This combination of graphite furnace AAS and hydride technology provides in-situ enrichment of mercury as well as the hydride forming elements arsenic, antimony, and selenium inside the graphite tube. Thus, the technique allows trace element analysis with detection limits as low as 0.005 µg/L.

Materials and Methods

In this application note, mercury and the hydride-forming elements arsenic, antimony, and selenium were analyzed in certified reference materials and drinking water using the HydrEA technique. The hydride system HS60 with continuous flow injection was coupled with an autosampler, allowing a fully automated analysis procedure. Combined with the graphite furnace AAS of the ZEE nit series, sensitive analysis of mercury and the hydride-forming elements was achieved. The analytes were preconcentrated in the graphite tube (wall type), which was coated with gold (for mercury) or iridium (for the hydride-forming elements). Subsequently, they were electrothermally atomized and analyzed. For comparison, a calibration curve for mercury and arsenic using the classical hydride technique with a quartz cell was also performed. In addition, cadmium and lead were determined via graphite furnace AAS with superior Zeeman background correction.

Samples and reagents

- Hydrochloric acid: $c(\text{HCl}) = 32$ (wt-%), $\rho(\text{HCl}) = 1.16$ g/mL
- Nitric acid: $c(\text{HNO}_3) = 65$ wt-%, $\rho(\text{HNO}_3) = 1.39$ g/mL
- Potassium iodide (KI) / ascorbic acid solution: $c(\text{KI}) = 500$ g/L, $c(\text{ascorbic acid}) = 100$ g/L
- NaBH_4 solution: 0.3 wt-% NaBH_4 and 0.1 wt-% NaOH in deionized water
- Solution for gold coating of the graphite tube: $c(\text{Au}) = 1$ g/L
- Solution for iridium coating of the graphite tube: $c(\text{Ir}) = 1$ g/L
- Pd/ $\text{Mg}(\text{NO}_3)_2$ -modifier for GF-AAS: $c(\text{Pd}) = 1$ g/L, $c(\text{Mg}(\text{NO}_3)_2) = 0.1$ g/L
- Certified reference material for Hg in water: CRM 1641d
- Certified reference materials for As, Sb, Se, Pb, and Cd in water: CRM 1640a and CRM 1643f

Sample preparation

The analysis of arsenic and antimony was performed according to ISO 17378-2:2014. Since only As(III) and Sb(III) react quickly and quantitatively under the conditions used in hydride technique, As(V) and Sb(V) have to be reduced to As(III) or Sb(III) prior to the step of hydride generation. This was assured by adding 15 mL of hydrochloric acid and 1 mL of KI/ascorbic acid solution to 25 mL of prediluted sample solution. After a reaction time of two hours at room temperature the mixture was filled up to a volume of 50 mL with deionized water. The blank sample and the standard solutions were prereduced in the same way.

The analysis of selenium was performed according to ISO/TS 17379-2:2013. Similar to arsenic and antimony, Se(V) has to be reduced to Se(III) prior to the step of hydride generation. For the prereduction of Se(V) to Se(III), 15 mL of hydrochloric acid were added to 25 mL of prediluted sample solution. The mixture was carefully boiled under reflux for one hour and then made up to a volume of 50 mL with deionized water. The blank sample and the standard solutions were prereduced in the same way.

For the analysis of mercury, the dilutions of the samples and the standards were prepared in 0.6 vol-% HCl and 0.3 vol-% HNO_3 . For the analysis of cadmium and lead, 0.5 vol-% HNO_3 was used as diluting solution for samples and standards.

Instrumentation

All measurements were carried out with the ZEE nit 650 P GF-AAS, equipped with an AS-GF autosampler. For mercury and the hydride forming elements, the flow injection hydride system HS60 with HydrEA upgrade kit and the AS-F autosampler were used additionally. The method parameters for the GF-AAS for all elements are shown in Table 1, the parameters for the hydride system in HydrEA mode for mercury, arsenic, antimony, and selenium can be found in Table 2. The method parameters for the hydride system in classical hydride mode with a quartz cell are shown in Table 3 for arsenic and in Table 4 for mercury.

Table 1: Method parameters for GF-AAS for all analytes

Element	Technique (graphite tube type)	Wave-length [nm]	Slit [nm]	Lamp current [mA]	T _{Drying} [°C]	T _{Pyrolysis} [°C]	T _{Atomizing} [°C]	Ramp [°C/s]	Modifier
Hg	HydrEA (wall)	253.7	1.2	3	65	-	950	1200	Gold coating
As	HydrEA (wall)	193.7	0.8	5	300	-	2100	1000	Iridium coating
Sb	HydrEA (wall)	217.6	0.2	7	300	-	2100	1000	Iridium coating
Se	HydrEA (wall)	196.0	1.2	6	300	-	2150	1000	Iridium coating
Cd*	EA (platform)	228.8	0.8	2	80/90/110	600	1600	1500	5 µL Pd/Mg(NO ₃) ₂
Pb*	EA (platform)	283.3	0.8	2	85/95/110	900	1900	1900	5 µL Pd/Mg(NO ₃) ₂

* Pb and Cd were measured in Zeeman 2-field mode with max. 0.8 T magnetic field strength.

Table 2: Hydride system parameters for mercury, arsenic, antimony, and selenium in HydrEA mode

Element	Load time [s]	Reaction time [s]	Purge time 1 [s]	Purge time 2 [s]	Transport solution	Reduction solution
Hg	20	20	30	7	3% HCl	0.3% NaBH ₄ + 0.1% NaOH
As, Sb, Se	20	20	35	5	3% HCl	0.3% NaBH ₄ + 0.1% NaOH

Table 3: Hydride system parameters for arsenic in classical hydride mode with quartz cell

Element	Load time [s]	AZ wait time [s]	Reaction time [s]	Purge time 1 [s]	Transport solution	Reduction solution
As	14	20	20	40	3% HCl	0.3% NaBH ₄ + 0.1% NaOH

Table 4: Hydride system parameters for mercury with and without enrichment in classical hydride mode with quartz cell

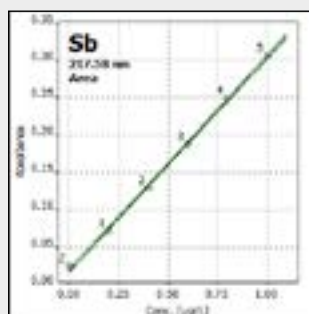
Element	Load time [s]	Reaction time [s]	Purge time 1 [s]	Purge time 2 [s]	Purge time 3 [s]	Heat time collector [s]	Cool time collector [s]	Transport solution	Reduction solution
Hg (without enrichment)	14	20	30	15	-	-	-	3% HCl	0.3% NaBH ₄ + 0.1% NaOH
Hg (with enrichment)	14	20	20	50	0	15	40	3% HCl	0.3% NaBH ₄ + 0.1% NaOH

Calibration

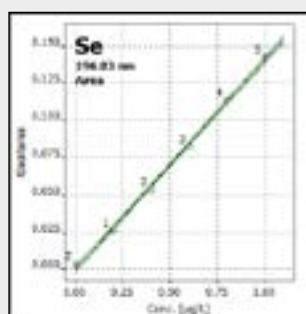
An external calibration with aqueous standards was performed for all analytes. The concentrations of the calibration standards are shown in Table 5. Figures 1a–d show the calibration curves with corresponding correlation factors R^2 and limits of detection (LOD) for antimony and selenium obtained by HydrEA technique, as well as for cadmium and lead obtained by graphite furnace AAS. Figures 2a–e shows a comparison of the calibration curves for mercury and arsenic, which were obtained by classical hydride technique with quartz cell and using the HydrEA technique.

Table 5: Concentrations of the calibration standards

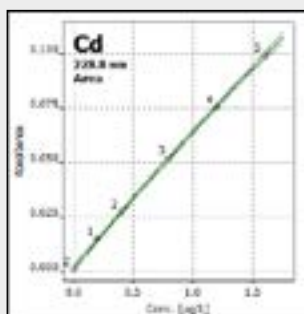
Standard	Concentration [$\mu\text{g/L}$]								
	Hg (HydrEA)	Hg (hydride w/o enrich.)	Hg (hydride w/ enrich.)	As (hydride)	As (HydrEA)	Sb (HydrEA)	Se (HydrEA)	Cd (GF-AAS)	Pb (GF-AAS)
Cal 0	0	0	0	0	0	0	0	0	0
Std. 1	0,1	0,5	0,2	0,5	0,2	0,2	0,2	0,2	6
Std. 2	0,5	1,0	0,4	1,0	0,4	0,4	0,4	0,4	12
Std. 3	1,0	2,5	0,8	2,0	0,6	0,6	0,6	0,8	18
Std. 4	1,5	5,0	1,6	4,0	0,8	0,8	0,8	1,2	24
Std. 5	2,0	-	-	8,0	1,0	1,0	1,0	1,6	30



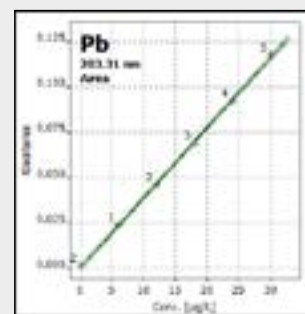
Evaluation by area
Linear, $R^2 = 0.9979$
LOD = 0.01 $\mu\text{g/L}$



Evaluation by area
Linear, $R^2 = 0.9960$
LOD = 0.01 $\mu\text{g/L}$

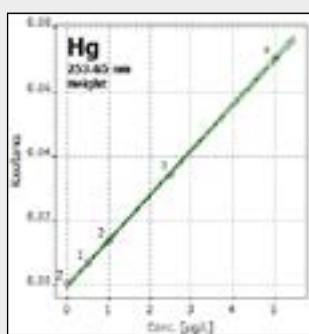


Evaluation by area
Non-linear rational, $R^2 = 0.9997$
LOD = 0.009 $\mu\text{g/L}$

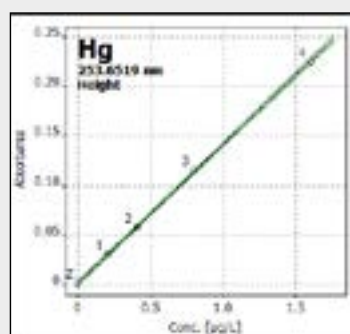


Evaluation by area
Linear, $R^2 = 0.9992$
LOD = 0.25 $\mu\text{g/L}$

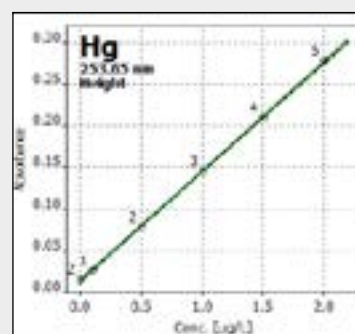
Figures 1a–d: Calibration parameters and limits of detection (LOD) for antimony and selenium with HydrEA technique and for cadmium and lead with graphite furnace AAS



Evaluation by height
Linear, $R^2 = 0.9997$
LOD = 0.05 $\mu\text{g/L}$
Classical hydride technique
without enrichment

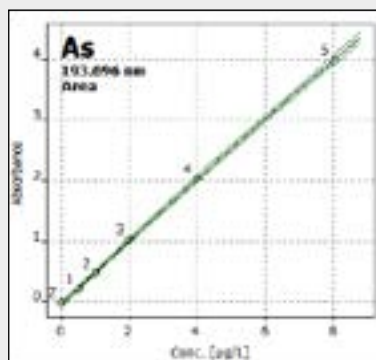


Evaluation by height
Linear, $R^2 = 0.9997$
LOD = 0.02 $\mu\text{g/L}$
Classical hydride technique
with enrichment on gold collector

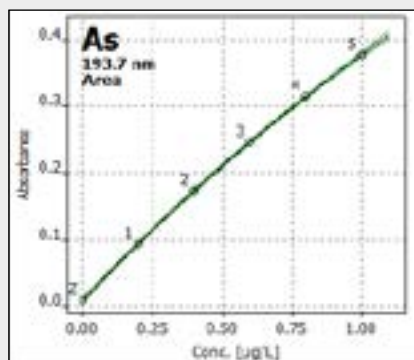


Evaluation by height
Linear, $R^2 = 0.9998$
LOD = 0.005 $\mu\text{g/L}$
HydrEA technique (hydride + GF-AAS)

Figures 2a–c: Calibration parameters and limits of detection (LOD) for mercury with classical hydride technique and HydrEA technique



Evaluation by area
Linear, $R^2 = 0.9997$
LOD = 0.05 µg/L
Classical hydride technique



Evaluation by area
Non-linear rational, $R^2 = 0.9999$
LOD = 0.005 µg/L
HydrEA technique (hydride + GF-AAS)

Figures 2d–e: Calibration parameters and limits of detection (LOD) for arsenic with classical hydride technique and HydrEA technique

Results and Discussion

All samples in this application note were analyzed by HydrEA technique and graphite furnace AAS. For the analysis of certified reference materials, very good recovery rates of the measured concentrations with the certified values could be achieved (93–109%, Table 6). The relative standard deviations for three replicate measurements were usually below 3%. In the drinking water sample, all analyte concentrations were below 1 µg/L. Excellent recovery values of 94–105% for spiked concentrations in the drinking water sample have been achieved (Table 7).

Table 6: Results for the certified reference materials

Sample	Element	Dilution factor	Certified concentration [µg/L]	Measured concentration [µg/L]	RSD [%]	Recovery of certified concentration
CRM 1641d	Hg	1000	1568	1520	1.3	97.4
CRM 1640a	As	10	8.075	7.51	0.5	93.4
	Sb	10	5.105	4.81	2.5	94.1
	Se	25	20.13	19.3	1.5	95.9
	Cd	10	3.992	4.37	3.4	109.3
	Pb	1	12.101	11.89	0.4	98.2
CRM 1643f	As	100	57.42	53.4	2.8	92.9
	Sb	100	55.45	53.6	1.5	96.7
	Se	25	11.700	12.2	5.6	104.2
	Cd	10	5.89	5.66	1.8	96.1
	Pb	1	18.488	17.16	0.9	92.8

Table 7: Results for drinking water and recovery rates for spiking experiments

Sample	Element	Dilution factor	Measured concentration [$\mu\text{g/L}$]	RSD of sample [%]	Spiked concentration increase [$\mu\text{g/L}$]	RSD of spiked sample [%]	Recovery rate [%]
Drinking water	Hg	2	< LOD	-	1.0	0.5	99.4
	As	2	0.77	1.4	0.6	1.2	94.0
	Sb	2	0.11	13.0	0.6	0.8	95.5
	Se	2	0.56	2.2	0.6	1.8	100.2
	Cd	1	< LOD	-	0.6	0.9	105.0
	Pb	1	0.92	23.4	9	0.7	104.5

Conclusion

The hydride system HS60 with continuous flow injection in combination with Analytik Jena's AAS instruments are reliable, easy to use, and therefore perfectly suited for analysis of mercury and the hydride forming elements arsenic, selenium, and antimony in the low $\mu\text{g/L}$ range. Coupling the hydride system with an AS-F autosampler allows complete automation of the analysis procedure and makes the application perfect for robust routine analysis. For the precise analysis of trace concentrations below $1 \mu\text{g/L}$, as frequently found in drinking water, the combination of the HS60 hydride system (with the autosampler AS-F) and graphite furnace AAS is an excellent tool. This so-called HydrEA technique unites the high atomization efficiency and sensitivity of graphite furnace AAS with the high selectivity of the hydride generation or cold vapor technique due to the complete separation of the interfering matrix. Limits of detection as low as $0.005 \mu\text{g/L}$ can be reached with this technique. Furthermore, traces of toxic elements such as lead and cadmium can be analyzed even in complex matrices using the graphite furnace AAS of the ZEE nit series with superior Zeeman background correction.



Figure 3: Hydride system HS60

References:

- [1] Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, OJ L 330, 5.12.1998, p. 32–54 (ES, DA, DE, EL, EN, FR, IT, NL, PT, FI, SV)
- [2] National Primary Drinking Water Regulations, United States Environmental Protection Agency
- [3] Verordnung über die Qualität von Wasser für den menschlichen Gebrauch (Trinkwasserverordnung - TrinkwV), 2001

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