APPLICATION

AAS 8

DETERMINATION OF HEAVY METALS FROM DUMP WATER (landfill leachate)

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For the control of landfill sites in Germany, the technical regulation „Waste" (TA Abfall [1]) is valid. A large number of different species of organic and inorganic nature can be found in the leaked water, which is coming out of refuse disposal sites. For the determination of heavy metals using atomic absorption spectrometry, the recognition and elimination of interferences is the main task. Since enrichment of heavy metals takes place in this landfill leachate, most of the elements can be measured in the mg/l (ppm)-range.

In this case, flame atomic absorption spectrometry is the method of the choice and offers simple and reliable measurements. However, for some elements, present in lower concentration, analysis must be performed using a graphite furnace system.

In our ealier work on slurries [1] we pointed out, that in such cases the use of the dual atomizer system AA-6701 gives economical advantages in comparison to ICP technique. This system allows to perform flame as well as furnace analysis in one unit without manual adjustments on low running costs.

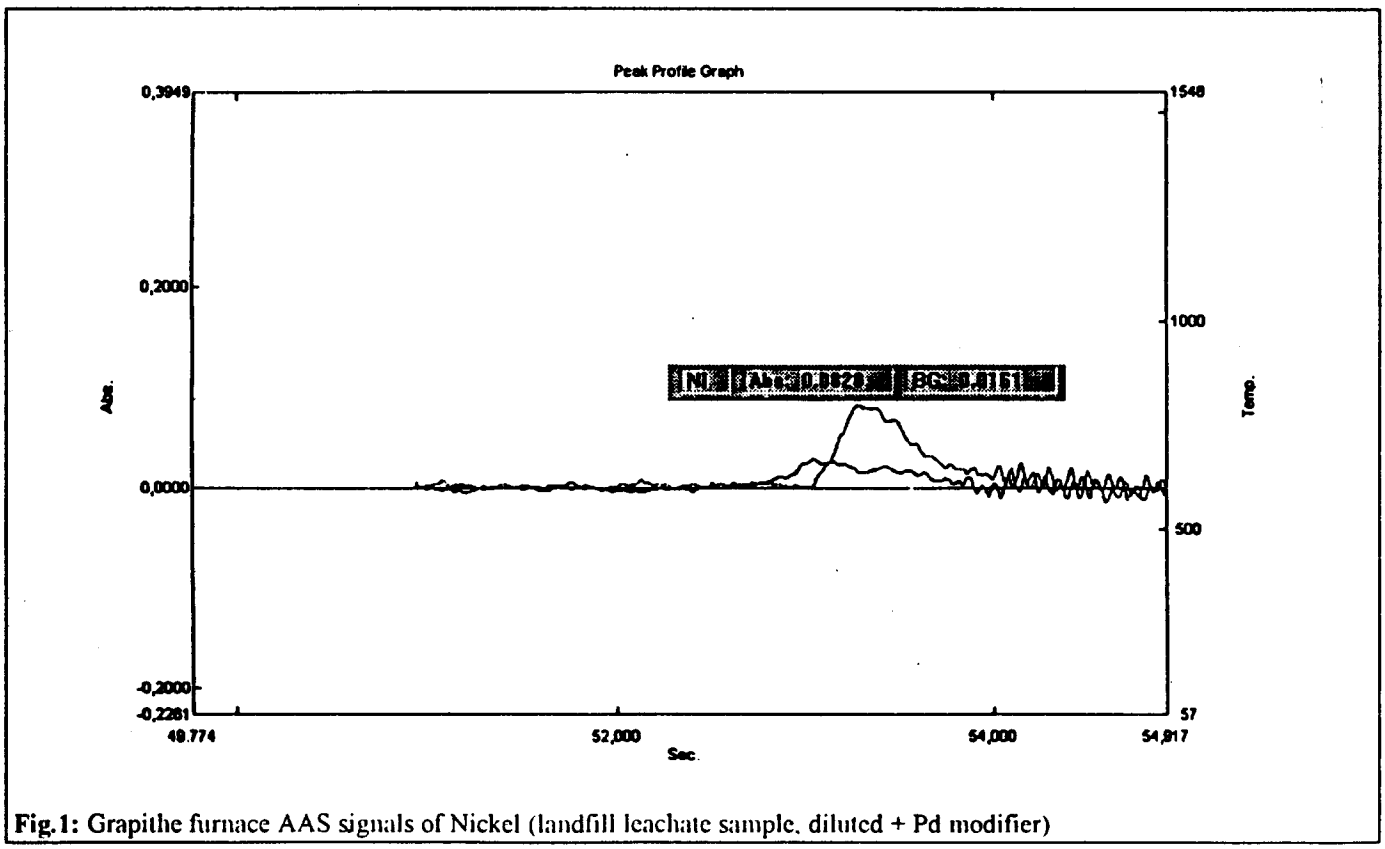

Fig.1: Grapithe furnace AAS signals of Nickel (landfill leachate sample, diluted + Pd modifier)

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For precise injection and automatization, the autosampler system ASC-6000 is recommended. In Full Auto mode and using the autosampler, multi-element sequences with up to 20 elements can be programmed and analysis will be performed with all necessary steps i.e. lamp warmup, line search, blank measurement and calibration for each element.

ASC-6000 can be used for furnace and flame operation (microsampling). Moreover, it is able to perform real dilution which is important in analyzing complex matrices in furnace since simple dilution is often used in matrix modification. In addition, the function „Autodilute and Reanalyse" is available to perform automatic adaption of the dilution range to the user-defined calibration range.

Analysis of landfill leachate

However, in most cases automatic dilution was not necessary to perform analysis in this examination. Since the autosampler operation will influence the analysis time, the autosampler have been used for injection and re-analysis only and remaining dilution processes have been performed manually prior to analysis.

For the analysis of heavy metals, six samples of leachate have been provided from a landfill of hazardous waste. These samples have been collected from wells of different deposit areas.

In graphite furnace mode, simple addition of palladium modifier and use of adapted furnace programs was sufficient to separate remaining background signals using D_2 - correction. In Fig.1 the signals during Nickel measurement of real sample of leachate is shown.

After orientation about occuring signals in graphite furnace over-night multi-element run it becomes clear, that most of the selected elemets could be measured using the simple and fast flame technique.Thus, the elements Manganese, Cadmium,Iron and Zinc have been analysed by flame and Chromium and Nickel were analysed by furnace. In addition, Arsenic measurements have been performed using hydride system HVG-1.

The operation of the function „Autodilute and Reanalyse" is explained in detail on the following example:

During determination of Chromium in graphite furnace, a prediluted sample aliquot (20 µl) from sample 16 and 17 was injected. The detected absorptions of 0.5806 and 0.5124 (see Tab.1) do not correspond to the specified calibration range (Fig. 2.) and result in wrong concentration readings, since the calibration curve has a significant curvature for higher absorbances.

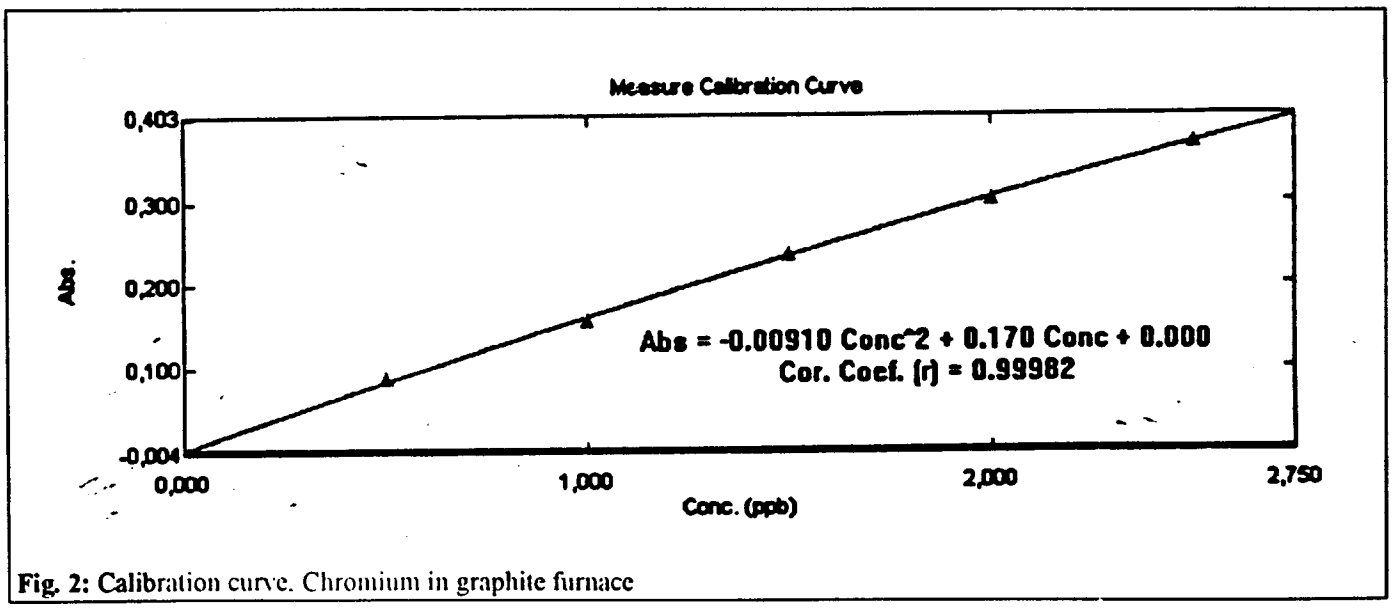

Fig. 2: Calibration curve. Chromium in graphite furnace

If the function „Autodilute and Reanalyse" is activated, the autosampler will stop the current measurement in this case. During direct injection procedures with prediluted samples, calculation of a smaller amount of sample in correspondance to the specified calibration range will be carried out, and a smaller aliquot amount of sample will be injected afterwards.
In mixing routines, the autosampler will waste the sample and start to prepare a new sample portion based on the calculated dilution factor. This dilution factor is reported in the measured result table.

	Sample ID	Abs.Signal	Background Signal D2	Dil. Factor Sample	Auto. Dil. Sample	Result Conc. in ppb	Inj.Vol. Sample µl
UNK	leachate well 16	***0,5806***	0,0683	10	1,0000	44,8897	20
UNK	leachate well 16	0,0790	0,0051	10	2,8570	13,6053	7
UNK-REP	leachate well 16	0,0757	0,0041	10	2,8570	13,0337	7
UNK-AVG	leachate well 16	0,0774	0,0046	10	2,8570	**13,3193**	7
UNK	leachate well 17	***0,5124***	0,0120	10	1,0000	37,7134	20
UNK	leachate well 17	0,1120	0,0037	10	2,8570	19,5122	7
UNK-REP	leachate well 17	0,1033	0,0020	10	2,8570	17,9530	7
UNK-AVG	leachate well 17	0,1077	0,0028	10	2,8570	**18,7313**	7

Tab. 1

In this way, routine analysis and multi-element sequences can run without interruption even if samples out of range are measured. The autodilute function is also available in flame analysis (microsampling).
The values in Tab.1 have been exported from measured result table of AAPC software to Excel.

Results of all analysis are summarized in the following table.

Elements	Mn	Cd	Fe	Zn	Zn	Cr	Ni	As
Concentration unit	mg/l	mg/l	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Atomization	Flame	Flame	Flame	Flame	Flame	Furnace	Furnace	HVG
Background compensation	D2	D2	D2	SR	D2	D2	D2	D2
Leachate well 12	0,33	<0,10	1,01	<10,00	<10,00	9,80	101,50	2,30
Leachate well 13	0,10	<0,10	0,78	22,30	35,50	27,90	1281,40	7,10
Leachate well 14	3,41	0,92	6,11	12,40	14,60	17,40	545,40	5,40
Leachate well 15	8,21	0,52	0,63	146,80	179,00	10,90	595,10	<1,00
Leachate well 16	0,24	0,13	<0,20	<10,00	<10,00	13,30	144,70	61,50
Leachate well 17	0 07	0,15	<0,20	27,00	31,10	18,70	21,60	5,70
Reference value Beckerath [3]		0,144	0,38-2700	20-27000	20-27000	18	14-30000	51

Tab. 2

High speed self reversal background compensation techniques was used in addition and for comparison purpose during the examination of Zinc, since spectral interferences arising from other elements can be expected in such samples. For detailed information about SR-technique see [2,4].

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The very different composition of each individual sample in comparison to the other samples is reflected in the result table. It is obvious, that these samples have been selected from different deposit areas. Unfortunately, there is no actual common data material available to compare with our results. In this situation we compare our data with results from an inquiry, performed by Beckerath in 1989 [3] as reference.
Examination of Manganese was also performed although this metal is not included in german regulation for deposit control, (see also reference values). It is our own experience, that Manganese is always present even in leachates of household refuse sites.
The presented AA-technique for the determination of heavy metals in landfill leachate and water, waste water and slurries is a cost saving alternative to ICP. The oppurtunities to perform flame as well as graphite furnace operation in multi-element routine analysis result in high lab efficiency and low running costs.

Literature:

[1] TA Abfall (German regulation)

[2] U.Oppermann und Dr.H. Hohmann, „Determination of heavy metals in sludges using AAS" Shimadzu Application Note AAS 3 (SCA-120-003E)

[3] Beckerath, K. „Verfahren zur Behandlung von Sickerwässern", Zeitschr.Entsorgungs-Praxis 7(9) Bertelsmann-Verlag 1989(published in german only)

[4] U.Oppermann, „Zn-Determination using high-speed self reversal technique" Shimadzu-Application Note AAS 1 (SCA 120-001E)

Instrumentation

Atomic-Absorption-Spectrophotometer	AA-6701
Autosampler	ASC-6000
Graphite furnace	GFA-6500
Hydride system	HVG-1

02/E/03/96/HH/HH/BFL

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