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EVALUATION OF DIFFERENT ANALYTICAL PROCEDURES IN THE TRACE ELEMENT ANALYSIS OF A LANDFILL LEACHATE

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ABSTRACT

In four groundwater samples taken at different depths near a waste disposal site at Noordwijk the trace-elements have been measured with different analytical procedures.

Subsequent recovery experiments are recommended to select the optimum analytical procedure for each type of groundwater sampled near the sites.

INTRODUCTION

Within the framework of an investigation of groundwater pollution near waste disposal sites, the quantitative determination of trace-elements at different depths was programmed. The concentrations of most trace-elements of interest could not be measured with methods normally used for groundwaters.

The main sources of interference in the trace-element analysis of groundwaters near sites are the relatively high concentrations of Fe, Na, K, Ca, and Mg (2). While the concentrations of these constituents can vary in the groundwaters sampled at different sites, no generally applicable procedure of analysis is available at this moment.

Guidelines in sampling, pretreatment of samples and analysis leading to acceptable results for groundwater samples taken near the same site can be given however.

EXPERIMENTAL

Sampling and preservation

To avoid precipitation of ironhydroxides, and at the same time occlusion of trace-elements in the precipitate, sampling in a nitrogen-gas atmosphere was necessary.

It was noticed that light induced precipitation, therefore black polyethene sampling material was used.

To prevent adsorption of the trace-elements on the wall of the bottle, samples were acidified with nitric acid to pH 2.

DIGESTION

The selected digestion techniques varied from so-called "open" techniques with aqua regia (A), hydrochloric acid (B), to a "closed" technique (C).

(A) - After addition of 10 ml aqua regia to 250 ml of the sample, the sample was boiled until the volume was reduced to approximately 200 ml. The sample was cooled and made up to 250 ml with distilled water.

(B) - An amount of 25 ml hydrochloric acid (conc.) was added to 250 ml of the sample, and treated further in accordance with A.

(C) - Into an acid digestion bomb (Parr 4745) an amount of 2.0 ml sample and 0.3 ml of nitric acid (conc.) was transferred. After closing the bomb the destruction was carried out at 140 °C during 4 hours. After cooling the content was transferred into a 50 ml measuring flask and made up to volume with distilled water.

Iron removal and preconcentration by complexing with APDC*) and DADDTC*).

A part of the digest (A) was treated with amylacetate to remove iron. Subsequently the trace-elements were preconcentrated with the chelating agents: APDC and DADDTC before measurement with the AAS-flame technique.

* APDC : Ammonium Pyrrolidine-dithiocarbaminate
DADDTC : Diethylammonium-diethyl dithiocarbaminate

ANALYSIS

The digests A, B and C have been measured with atomic absorption spectrometry (AAS) using flame-(I), hydride generating-(II) and graphite furnace techniques (III) The operating conditions are mentioned in tables 1 and 2.

The reduction reagent, forming the AsH_3 (hydride) was supplied as 2,5 ml of a solution containing 10% $NaBH_4$ and 2,5% NaOH.

The formed hydride was purged with argon into the quartz measuring cell (cuvet) which was heated at 1000 °C (program 1). The arsenic, from the dissociated AsH_3 was measured with the operating conditions mentioned in Table 1.

The elements: Pb, Cu, Cd were also measured with Differential Pulse Anodic Stripping Voltammetry, to compare the results with the AAS data.

RESULTS AND DISCUSSION

The same analytical procedures have been performed after addition of a known amount of the element of interest to the sample. The recovery of the concentrations found have been expressed as the percentage of the quantity added (Table 3). The results indicate that with certain combinations of digestion and analytical procedures acceptable quantities of the additions have been recovered (90-105%).

The low concentrations and recoveries measured after removal of iron and complexation with APDC and DADDTC suggest that this method (I*) is not applicable to groundwaters with relatively low concentrations of trace- elements. On landfill leachates from Delden and Tilburg, with concentration of trace-elements that are 10-30 times higher than in the groundwater studied, the method was successfully applied however (3).

CONCLUSION

For the main part of the trace-elements different concentrations have been found depending upon the analytical procedure applied. Regarding the results of other laboratories it seems that methods leading to acceptable results cannot always be used for the analysis of groundwater samples taken from other sites. With respect to quantitative trace-element analysis it is recommended therefore that groundwater samples taken from the same site should be checked with different analytical procedures. At least the digestion-procedures A, B, C and the analytical technique I(*), II and III, described in this paper, should be tested. Subsequent recovery experiments should be performed in order to select the optimum analytical procedure.

REFERENCES

1 H. Mooy, P. Eng. Procedures for the analysis of Landfill Leachate Appended Seminar Proceedings Report. E.P.A., Vancouver, 1975.
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3 W.M. Martens, Investigation of a determination method for a number of trace-elements in Landfill Leachate, Intern. report of the National Institute for Public Health, Bilthoven, mr. 127/77 lmc, June 1977.

TABLE 1

Operating conditions for the determination of Zn, Fe, Li, K, Na, Ca and Mg by flame-atomic adsorption and of As by the hydride generating technique (MHS-1) Perkin-Elmer

	Measurements with flame techniques (I)							Hydride generating Technique (II)
Element	Zn	Fe	Li	K	Na	Ca	Mg	As **
Wavelength (nm)	213.9	248.3	670.8	766.5	589.0	422.7	285.2	193.7
Slit (nm)	0.7	0.2	1.4	1.4	1.4	1.4	0.7	0.7
Background correction (Deuterium arc)	+	+	-	-	-	-	+	+
Flame composition acetylene/air (A/A)	A/A	A/A	A/A	A/A	A/A	A/A	A/A	-
Burner angle (degrees)	0	0	0	90	90	90	90	- cuvet
Sensitivity (in mg/l for 1% absorption	0.02	0.1	0.03	0.6	0.6	1.8	0.2	3×10^{-5}
Addition of C_s (1 ml, 20% sol./100 ml sample)	-	-	-	+	+	-	-	-
Addition of La (1 ml, 10% sol./100 ml sample)	-	-	-	-	-	+	+	-

**) The sample obtained after digestion with hydrochloric acid (method B) was diluted 20 times. About 24 hours before the measurement of arsenic in this sample, 5 ml HCl (6%) 0.25 g KJ and 0.25 g ascorbic acid were added to 20 ml of the diluted sample as a prereductant.

TABLE 2

Operating conditions for the determination of Cu, Cd, Pb, Ni, Co, Mn by graphite furnace technique (III) (P.E. 603) and HGA 74

Element	Cu	Cd	Pb	Ni	Co	Mn
Wavelength (nm)	324.7	228.8	283.3	352.5	240.7	279.5
Slit (nm)	0.7	0.7	0.7	0.2	0.2	0.2
Background correction (Deuterium arc)	+	+	+	-	+	+
Charring temperature (°C)	900	300	700	1200	1000	1000
Atomization " (°C)	2650	1900	2100	2650	2650	2500
Injection volume (μl)	50	50	50	50	50	50
Sensitivity (in nanograms for 1% absorption)	0.02	0.003	0.11	0.14	0.03	0.02
Pyrolytic coated graphite tube (lanthanumcarbide)	+	-	-	+	+	-
Addition of 1 ml 5% Ni sol./100 ml sample	-	-	+	-	-	-

Table 3

Element	Applied method of Digestion	Analysis	Concentration of element in µg/l found in samples from Noordwijk at 4 different depths				Percentage of addition recovered
			1	2	3	4	
As	C	III	13	50	30	13	80
	B	II	22	62	42	27	90
Cu	B	III	60	85	55	90	105
	A	III	70	80	50	80	115
	A	I*	46	50	25	48	55
Cd	C	III	7.5	5	5	2.5	100
	A	I*	4	2	2	2	50
Pb	C	III	50	125	119	69	96
	A	I*	<20	<20	<20	<20	
	A	DPASV**	45	115	110	70	90
Ni	B	III	50	80	80	80	92
	A	I*	50	60	50	40	90
Zn	A	I	410	520	580	200	98
	A	I*	330	420	430	130	75
Co	C	III	25	75	75	25	100
	A	I*	10	40	40	20	55
Fe	A	I	58x 10^3	62.5x10^3	59x 10^3	59	94
	C	III	57.5x10^3	62.5x10^3	57,5x10^3	60	90
	C	I	55x 10^3	60x 10^3	55x 10^3	57.5	92
Li	A	I	260	395	480	375	98
	C	I	250	375	462.5	369	90
Mn	A	I	1400	2100	700	1850	91
	C	III	1675	2300	800	2175	93
	A	I*	1150	1760	530	1440	75
K	A	I	590x 10^3	730x 10^3	840x 10^3	590x 10^3	96
Na	A	I	1500x10^3	1700x10^3	2350x10^3	1600x10^3	100
Ca	A	I	350x 10^3	300x 10^3	300x 10^3	410x 10^3	96
Mg	A	I	170x 10^3	185x 10^3	200x 10^3	210x 10^3	98

I* Flame technique after extraction with amylacetate and complexing with APDC and DADDTC

** Differential pulse anodic stripping voltammetry