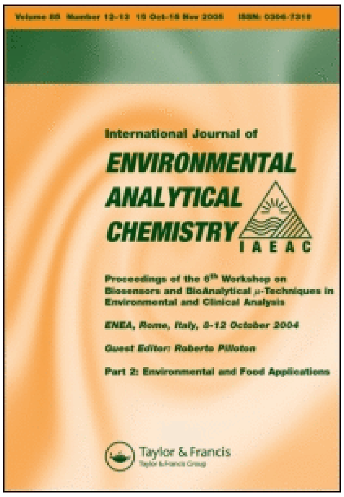

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Determination of Some Heavy Metals in the Dead Sea

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Determination of Some Heavy Metals in the Dead Sea

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Chemical interferences in determination of trace heavy metals in a concentrated salt matrix like the Dead Sea and the ways to overcome them, is the object of this paper. Three different methods were checked for this matter: APDC-TCTFE extraction with GFAAS, direct determination by AAS with matrix modifier and Zeeman background correction and anodic stripping at the level of ng/mL. Chemical blank and recovery studies were performed concerning each method.

KEY WORDS: Heavy metals, dead sea, extraction, GFAAS, Zeeman AAS, anodic stripping voltametry, differential pulse polarography.

INTRODUCTION

Determination of trace heavy metals in concentrated salt matrices as the Dead Sea brine, is a very difficult task. In a previous paper we tried to perform this determination by GFAAS.[8] In the present paper, we report about our experiments to perform this analysis by three different ways: Extraction by APDC-TCTFE and GFAAS, direct analysis using Zeeman background correction ASS and anodic stripping voltametry with differential pulse polarography. In the recent literature there are indications about utilization of these techniques for sea water analysis.[1–7]

EXPERIMENTAL

Instruments

A Perkin-Elmer Zeeman/5000 equipped with an AS-40 autosampler and a strip-chart recorder Yokogawa Type 3046 were used for determinations. Data were collected (out of the strip-chart recorder) by a Perkin-Elmer 3600 Data Station. Extracted element concentrations were reported by the ASDMS (PE Part No. 0057-2785) software package and printed out on a Perkin-Elmer PR.660 printer. For the Zeeman system peak absorbance and integrated peak absorbance were calculated with the HGA graphic software (PE. Part No. 0047-0686). Pyrolytically coated tubes, Perkin-Elmer Part No. 0109-322 were used. The integration time was 6 sec. Two series of signals were recorded: Zeeman background corrected -ZAA and single beam-SB for the background determination. The data were stored on a Digital VAX 750 computer, for later use.

Polarographic determination was performed on a Metrohm Polarecord E 506 equipped with a Polarography Stand E 505 containing a DME electrode and a HME. For AVS electrolysis, the times were controlled by a Metrohm Model 621 timer.

MATERIALS

The Dead Sea brine samples were provided by ORMAT, the first solar pound research group of Israel, which performs a continuous survey on Dead Sea. Each sample was stabilised with conc. HNO_3 (Merk, Dithizone tested quality Art. 456) to pH 1.2 and stored at 15°C. Synthetic sea water was prepared using AR reagents in the way described in our previous paper.[8]

Stock solution of different metallic elements were prepared from chemical pure metals, dissolved in AG HNO_3 0.1 M. From the stock solutions, working solutions were prepared freshly every week in 0.1 M HNO_3 and further diluted as needed.

APDC (Ammonium 1-Pyrrolidinedithiocarbamate) of Aldrich Chemical Lot No. 5114 was prepared freshly every week and previously purified by extraction with TCTFE.

TCTFE (1,1,2-trichlortrifluorethan) of SG Merck Art. No. 8239 was used as solvent.

Three stage purified water (TPW)-deionized on Zelion Israel column, purified on active carbon and Seradest ion-exchanger system, was used for dilutions.

To avoid contaminations, the plastic and glassware was cleaned by sinking for 48 h in 5% HNO_3, rinse with deionized water five times rinse with TPW five times and dried at 118°C in an drying oven.

PROCEDURES

1) **Extraction with APDC and TCTFE and analysis by GFAAS:** To 100 mL of original or diluted Dead Sea brine or synthetic sea water 1 mL of extractant (a mixture 1/1 of 0.5% APDC and acetic buffer pH 4) is added and extracted twice with 10 mL TCTEE. The re-extraction from the organic phase was performed by adding 100 μL conc. HNO_3 and 4.9 mL TPW. For analysis working curves were used; for recovery studies, the samples were spiked with 1.5–7.0 ng/ml Cd, 15–30 ng/mL Cu and 15–30 ng/mL Pb respectively. The analysis were performed by GFAAS in a SB mode. Instrumental conditions are summarized in Table I.

2) **Direct analysis:** Acidified samples of Dead Sea brine and synthetic sea water diluted 1/10 with TPW were analysed by GFAAS with and without matrix modifiers. To a volume of 20 μL sample or an equivalent volume of 0.5 M $(NH_4)_2HPO_4$, 0.5 M $(NH_4)_2HPO_4 + HNO_3$ 8% or 1% NH_4NO_3 was added. Determination of heavy metals was preformed by internal standard, using the same instrumental conditions described in Table I.

3) **Anodic stripping voltametry with differential pulse polarography:** Electrochemical cells were cleaned in the same way used for plastic and glassware. A volume of 20 mL of original or diluted Dead Sea brine or synthetic sea water, was purged with nitrogen for 30 min. before analysis. In each experiment the deposition was performed at −1.0 V for 30 min. during continuous stirring. After 30 s quiescent period, the positive scan was started. A 5 mV/s scanning rate was used for the determination. In the given conditions, the half wave potential of the metals were: Cd: −0.512 V, Pb: −0.320 V, Cu: −0.020 V. Calibration was performed by standard addition.

TABLE I

Instrumental conditions for trace metal determination in the Dead Sea.

Parameters		Cd	Cu	Pb
Wavelength nm		228.8	324.6	283.3
Light source		HCL	HCL	HCL
Graphite tube		pyrocoated		
Matrix modifier		20 μL ammonium phosphate or nitrate		
Sample volume		20 μL		
HGA program				
Drying	Temp.°C	130	130	130
	Ramp(s)	30	30	30
	Hold(s)	30	30	30
Charing	Temp.°C	400	600	500
	Ramp(s)	30	25	30
	Hold(s)	30	30	30
Atomization	Temp.°C	1500	2500	2400
	Ramp(s)	1	1	1
	Hold(s)	5	5	5
	Int. flow (mL/min)	50	50	50
	Read	+	+	+
	Record	+	+	+
Cleaning	Temp.°C	2700	2700	2700
	Ramp(s)	1	1	1
	Hold(s)	1	1	1

RESULTS AND DISCUSSION

1. APDC-TCTFE extraction method

Calibration graphs were prepared for Cd, Cu and Pb by extraction of spiked TPW samples. The correlation coefficients shows a good recovery (Table II). For the Dead Sea brine the extraction was performed in a range of salinity of 0–320 g/L (the total salinity content of the Dead Sea) as it can be seen in Table III. The optimal salinity for the extraction is 128 g/l what means a ratio of 40 p DSB/60 p TPW. Extraction of TPW, 0.1 M nitric acid and spiked TPW with two different concentrations of Cd, Cu and Pb was performed, in order to obtain a representative value for the chemical blank. The results are summarised in Table IV.

The significant higher values obtained for spikes during the extraction process make us to conclude that there is a certain contribution of trace metals coming from the reagents' impurity.

TABLE II

Element	Correlation coefficient
Cd	0.997
Cu	0.999
Pb	0.994

TABLE III

Dead Sea brine extraction by APDC-TCTFE method.

Ratio					
Dead Sea brine mL	TPW mL	Total salinity g/L	Cd ng/mL	Cu ng/mL	Pb ng/mL
0	100	0	0.03	16.23	18.59
40	60	128	10.28	38.01	26.40
60	40	192	1.44	20.19	18.59
80	20	256	1.81	31.58	17.47
100	0	320	5.49	5.34	10.78

TABLE IV

Chemical blank by APDC-TCTFE extraction.

Sample	Cd ng/mL	Cu ng/mL	Pb ng/mL
TPW	0.016	4.52	0
0.1 M HNO_3	0.010	0	0
TPW + 3 ng Cd	3.0	21.0	22.0
TPW + 7 ng Cd	6.0	30.0	25.0
TPW + 15 ng Cu	4.0	4.0	29.0
TPW + 30 ng Cu	9.0	9.0	30.0
TPW + 15 ng Pb	1.0	1.0	37.0
TPW + 30 ng Pb	21.0	37.0	92.0

Synthetic Sea water extraction: The synthetic sea water was prepared based on the data described in our previous paper.[8] Extractions were performed on diluted samples (salinity 128 g/L) on spiked and nonspiked samples. The Cd and Pb recoveries gave not conclusive results. For Cu a good recovery was achieved as it can be seen in Figure 1. There is no correlation between standard added and the recoveries obtained for any metal analysed. For illustration, in Table V we summarized the results obtained for trace metal content in three different Dead Sea samples.

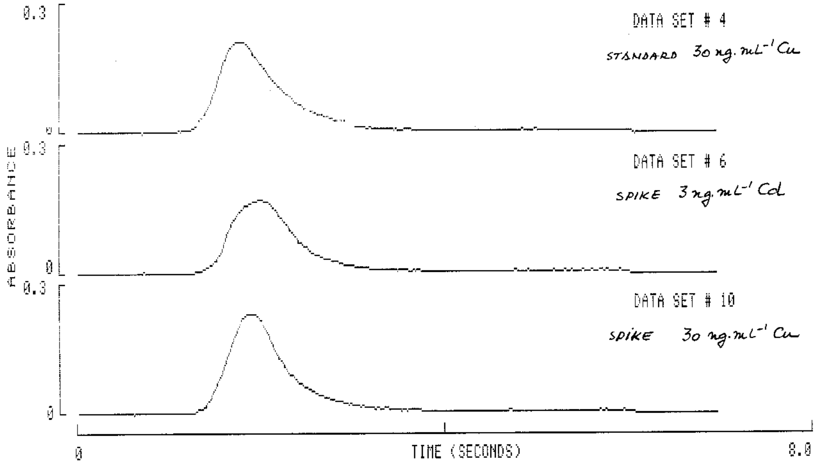

FIGURE 1 Determination of Cu by ZAA in synthetic sea water using APDC-TFTCE extraction.

TABLE V

Heavy metal content of Dead Sea brine by APDC-TCTFE method.

Sampling date site	Depth m	Cd ng/mL		Cu ng/mL		Pb ng/mL	
		Added	Found	Added	Found	Added	Found
18.10.82	0	—	2.02	—	20.27	—	7.72
Mishmar 50		1.5	1.63	30	20.59	30	12.10
19.06.84	0	—	0.38	—	7.10	—	0.02
North DS		1.5	0.65	30	10.73	30	0.03
15.10.84	2	—	8.61	—	37.54	—	23.45
Ein Gedi		1.5	1.49	30	—	30	21.36

2. Direct analysis by Zeeman AAS

The direct determination of Cd by ZAA led to no conclusive results, due to the fact that the spiked samples are drifted and suppressed see Figure 2–1, 2–2. Addition of 0.5 M $(NH_4)_2HPO_3$ as matrix modifier, has improved the results somehow but the quantitation is difficult to make for the same reason of drifting, as it can be seen in Figure 3–1, 3–2. Using the single beam mode of measurement (SB), the matrix signal overlaps the whole absorption peak. See Figure 4. The absorption peak of Cu is completely suppressed by the matrix in both ZAA or SB modes when no matrix modifier is added see Figure 5. Significant results were obtained by addition of 20 μL 0.5 M $(NH_4)_2HPO_4$ using internal standard addition. The results are one order of magnitude higher than those obtained by extraction: Dead Sea—Mishmar 50 *160 mg/mL* and Dead Sea–Ein Gedi *240 mg/mL.* In the SB mode both Cd and Pb are totally suppressed. Using matrix modifier in ZAA mode a measurable signal is present. The quantitation is doubtful because the matrix modifier itself has a signal similar with the sample Figure 6, 6–1. By addition of the lead standard, any increase in signal was recorded (Figure 7). It has to be emphasized that this phenomenon happens in spite of the fact that this system contains, in addition to the matrix modifier, a significant amount of magnesium, which is known as a matrix modifer for lead determination in saline system too.

We tried to use NH_4NO_3 1% as matrix modifier, too. The results are very much the same with whose obtained with $(NH_4)_2HPO_4$. Cd and Pb can not be quantified. The Cu was determined by standard addition method: Dead Sea Mishmar 50 *50 ng/L.* Dead Sea Ein Gedi—*30 ng/mL.* The results are an order of magnitude less than those obtained by the direct GFAAS method with phosphate.

Addition of 8% HNO_3 to the phosphate modifier as it is recommended by the team of Dr. Slavin[9] for sea water, did not improve the results.

3. Anodic stripping voltametry with differential pulse polarography

The influence of the salinity content on the polarographic wave of Cd, Cu and Pb was studied for a range of salinity of 32–320 g/L, at

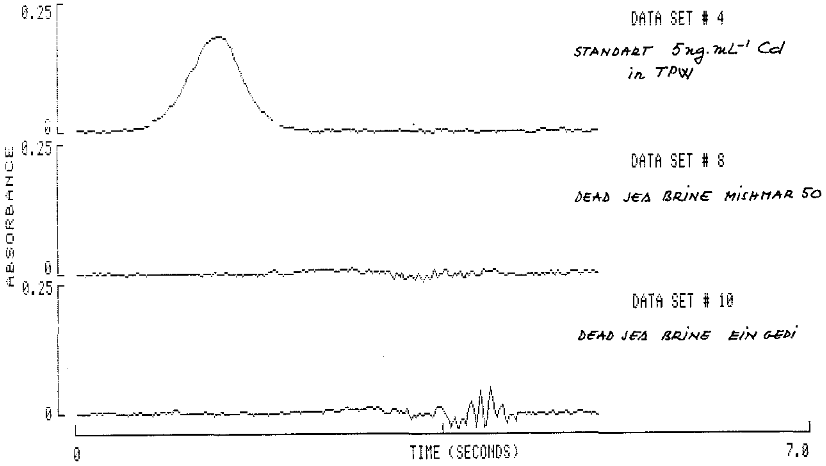

FIGURE 2-1 Direct determination of Cd by ZAA in 1/10 diluted Dead Sea brine.

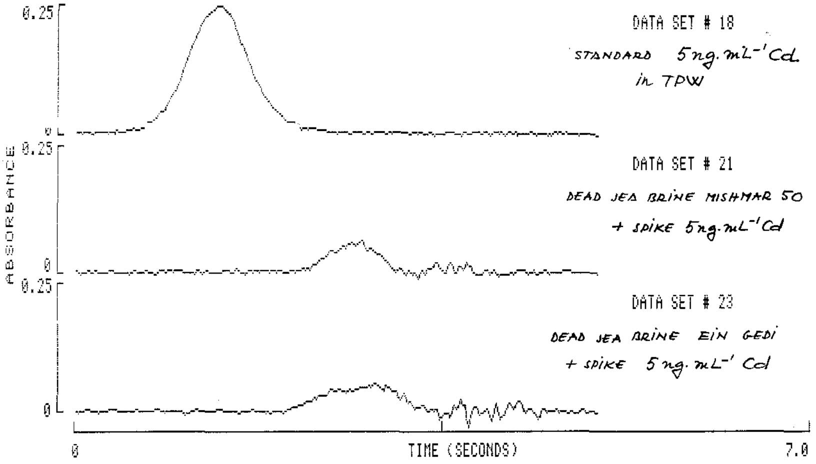

FIGURE 2-2 Direct determination of Cd by ZAA in 1/10 diluted and spiked Dead Sea brine.

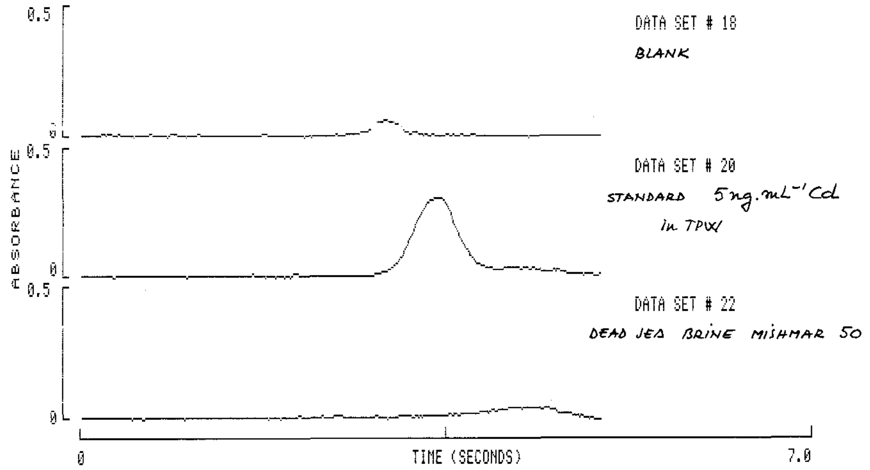

FIGURE 3-1 Direct determination of Cd by ZAA in 1/10 diluted Dead Sea brine with phosphate matrix modifier.

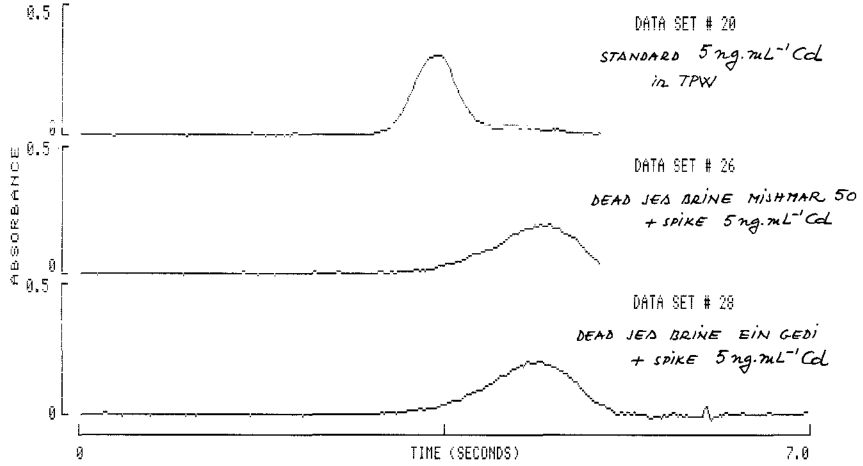

FIGURE 3-2 Direct determination of Cd by ZAA in 1/10 diluted and spiked Dead Sea brine with phosphate matrix and modifier.

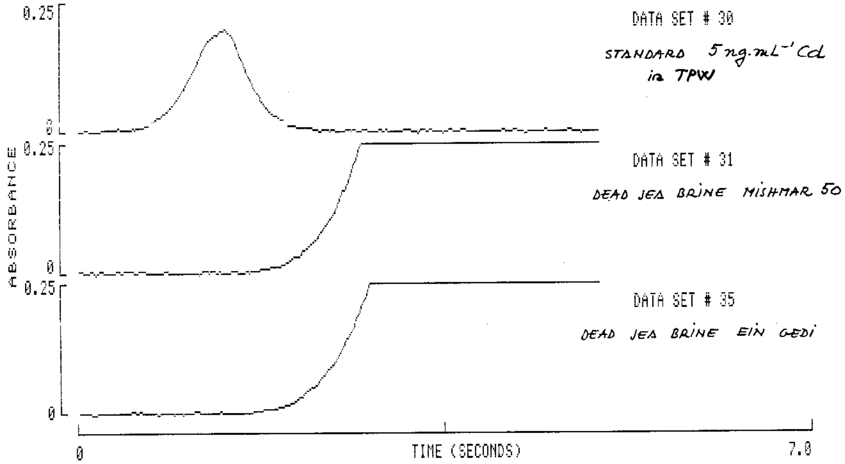

FIGURE 4 Direct determination of Cd by SB in 1/10 diluted Dead Sea brine.

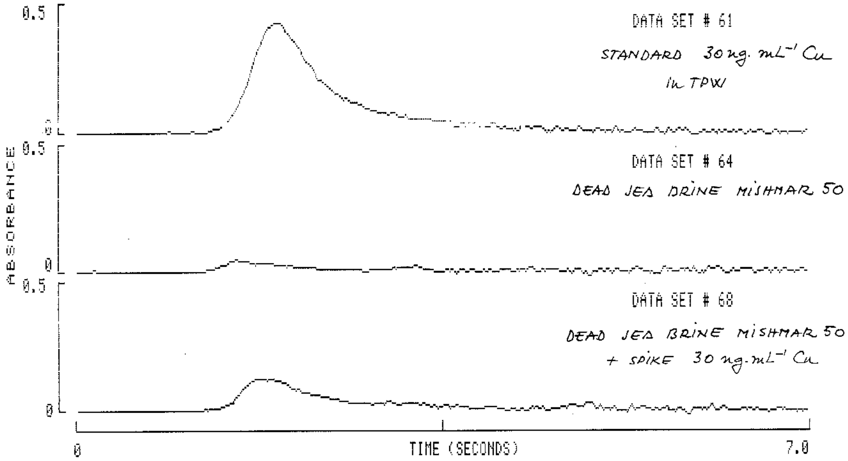

FIGURE 5 Direct determination of Cu by SB in 1/10 diluted Dead Sea brine with spiking.

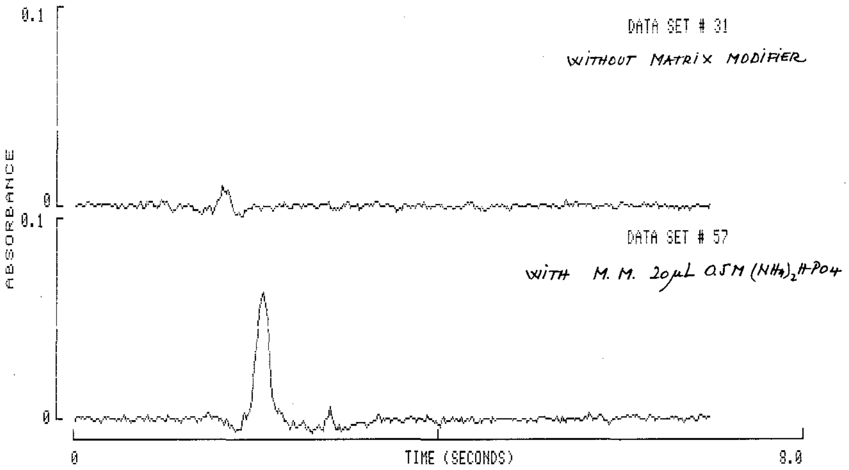

FIGURE 6 Direct determination of Pb by ZAA in 1/10 diluted Dead Sea brine in presence of phosphate matrix modifier.

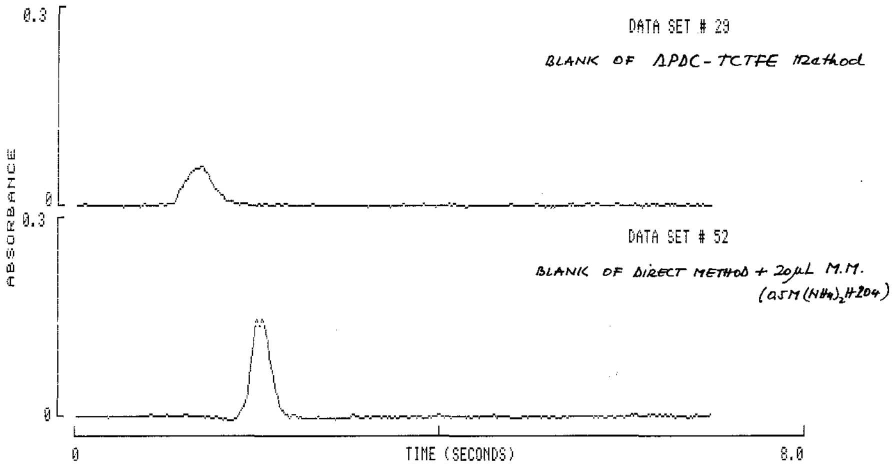

FIGURE 6-1 Pb absorption peaks for blanks in the extraction method and in the direct method with phosphate matrix modifier.

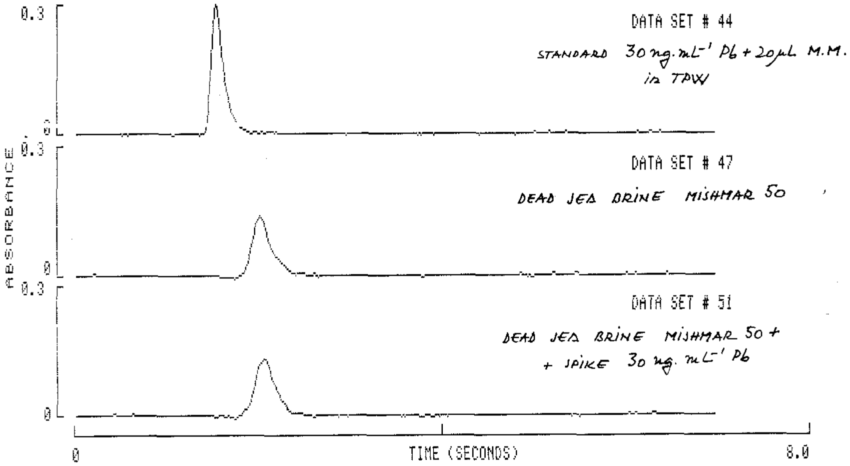

FIGURE 7 Direct determination of Pb by ZAA in 1/10 diluted Dead Sea brine using phosphate matrix modifier and internal standard.

two different deposition times of 20 min. and 30 min. respectively. The results are represented in Figure 8 and Figure 9. For Cu an increase of current was recorded until 210 g/L salinity. For lead, the current has a slight increase in the range of salinity of 210–260 g/L. We chose for determination, the salinity content of 210 g/L (14 mL DSB + 6 mL TPW). The determinations were performed using standard addition method and the results obtained, are summarized in Table VI.

TABLE VI

Trace heavy metals by ASVDP.

DDB sample	Depth m	Cd ng/mL	Cu ng/mL	Pb ng/mL
Ein Gedi	0	0.036	8.71	0.18
North DD	0	0.34	3.43	2.64
North DD	0	—	6.43	4.00
Mishmar	10	—	—	0.035

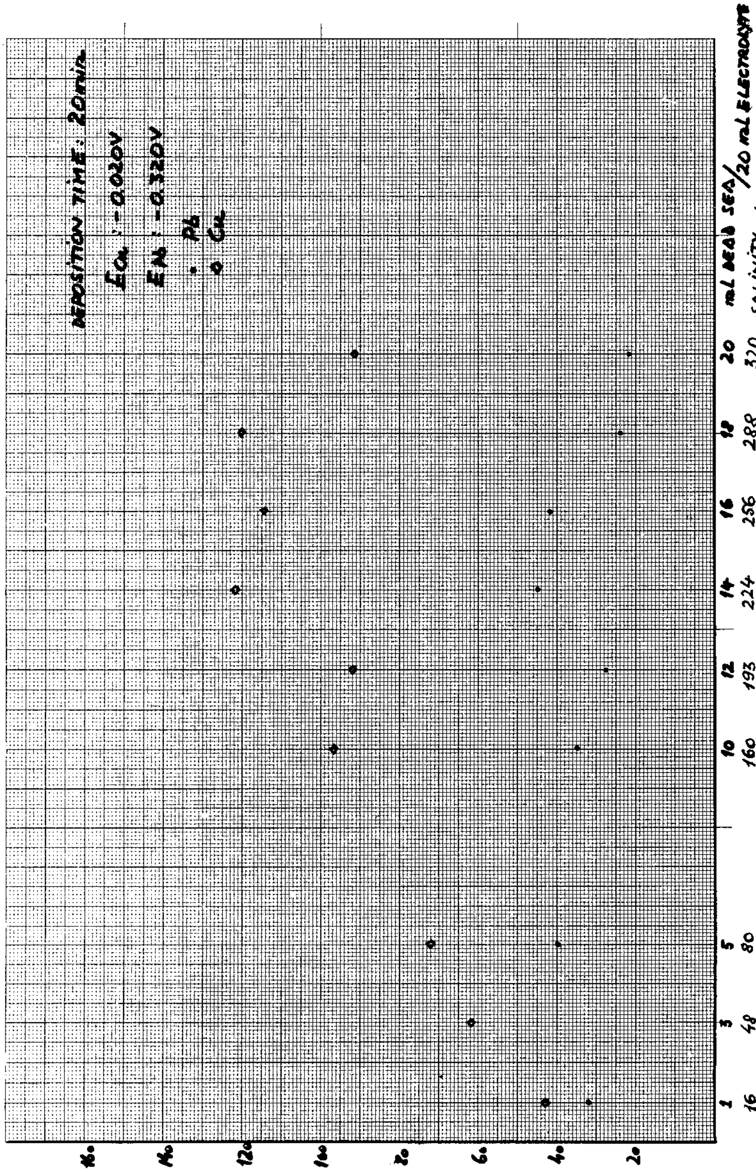

FIGURE 8 Influence of the Dead Sea salinity on the diffusion current of Cu and Pb at a deposition time of 20 min.

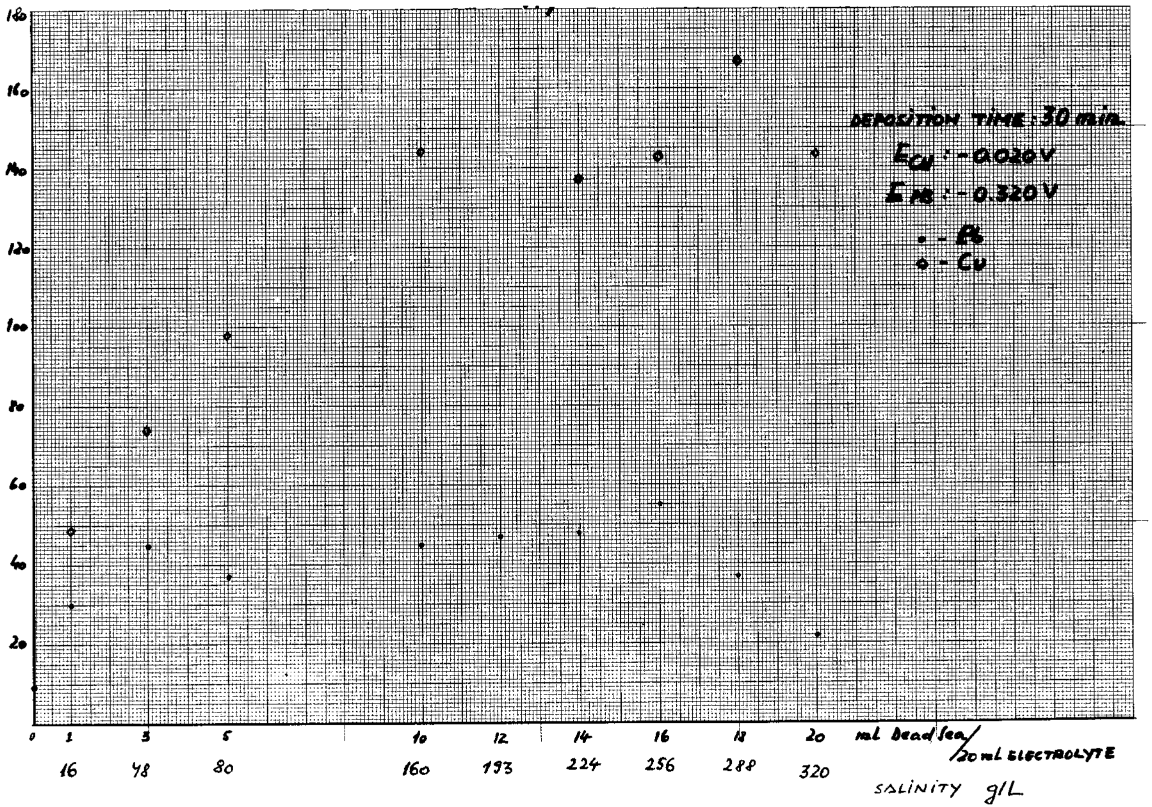

FIGURE 9 Influence of the Dead Sea salinity on the diffusion current of Cu and Pb at a deposition time of 30 min.

CONCLUSIONS

Determination of traces of Cd, Cu and Pb in the concentrated salt matrix of the Dead Sea brine by APDC-TCTFE extraction gives unreliable results. By direct determination using matrix modifiers as ammonium phosphate or ammonium nitrate in presence of already existent excess of magnesium good results were obtained for Cu. Chemical interference recorded by the determination of Cd and Pb can not be overcome even by use of Zeeman background correction. The ASVD method seems to be the most suitable for our proposal. It has to be emphasised that any procedure for elimination of organic materials was used during the sample preparation.

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