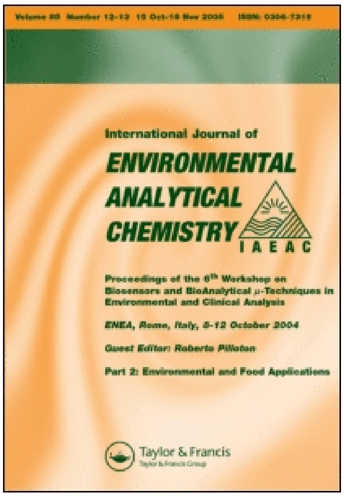

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Metal Analysis in Difficult Materials with Platform Furnace Zeeman-Atomic Absorption Spectrometry

I. Direct Determination of Cadmium in Crude Oil and Oil Products

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A method for the direct determination of extremely low cadmium levels in crude oil and oil products is described. By use of a Perkin-Elmer 5000-Z with HGA 500, L'vov-platform and oxygen ashing, detection limits of $<0.06\,\mu g$ Cd/l for crude oils and $<0.03\,\mu g$ Cd/l for Diesel- and carburetor fuels could be achieved. The temperature programme required for optimal results, is described and its evaluation discussed. The day-to-day precision for $0.3\,\mu g$ Cd/l is ±12%; the accuracy of the results, at least for samples with higher cadmium levels, was confirmed by comparison with DPASV after wet digestion and with GFAAS after extraction with dilute nitric acid. Different evaluation modes were applied and compared.

The cadmium contents found in various oils and oil products clearly show that a noticeable cadmium-contamination of the environment by combustion of crude oil and fuels is not to be expected.

KEY WORDS: Cadmium, oil, direct determination, charring with oxygen, Zeeman Graphite furnace Atomic Absorption Spectrometry.

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INTRODUCTION

If toxic heavy metals in the total environment are concerned, Cadmium requires particular attention. Even at rather low concentration levels it can produce irreversible adverse effects and in the human body it is considerably accumulated in kidneys, liver etc. in occupationally nonexposed persons predominantly via the food chain.[1,2]

The following anthropogenic sources cause the most important cadmium pollution of the environment:[2,3]

1) Iron- and steel industry as well as non-ferrous-metal industry.
2) Combustion of fossile fuels.

The levels of cadmium and other toxic metals in brown- and pitcoal are already well known.[2,4] The topic of this work therefore was the investigation of cadmium-contents in crude oil and oil products. This, however, hitherto constituted a difficult analytical task. First, the cadmium-values are extremely low and thus any analytical procedure became highly susceptible to contamination. Second, the commonly required wet digestion of the oil matrix was time consuming and difficult. Thus a direct determination with the aid of rather new methodological concepts would be the optimal approach. It has been shown recently that by application of modern graphite furnaces with L'vov-platform and oxygen addition during the charring step complex matrices could be directly analysed without external sample preparation.[5,6] Therefore, using such a technique and Zeeman compensation, an analytical procedure for the rapid, precise and accurate cadmium determination in crude oil and oil products could be evaluated. It achieves detection limits $<0.06\,\mu g\,Cd/l$ for crude oil and $<0.03\,\mu g\,Cd/l$ for Diesel- and carburetor fuels. Subsequently, this procedure and its evaluation is described in detail and examples for its application are given.

MATERIALS AND METHODS

Oils and oil products

The following products were investigated: carburetor fuels, Diesel fuels, light and heavy fuel oils, and crude oils from Arabia, Libya, Nigeria and the North Sea.

Apparatus

Perkin-Elmer 5000 Z; HGA 500 with Autosampler AS 40; Cd-EDL (5 W); Perkin-Elmer Data Station 10; Graphite tubes coated with pyrocarbon; L'vov platform.

Instrumental settings

Atomic absorption line: 228.8 nm
Slit: 0,7 nm
Sample size: 10–20 μl
The temperature programme is given in Table 1.

TABLE I
HGA temperature programme for direct cadmium determination in crude oil and oil products

Step	*T* °C	Ramp time s	Hold time s	Int. gas flow ml/min
1	150	10	0	300 0_2
2	250	60	0	300 0_2
3	530	200	100	50 0_2
4	530	1	39	300 Ar
5	530	1	2	0 Ar
6	1900	1	5	0 Ar
7	2400	1	3	300 Ar
8	20	1	9	300 Ar

Note: The given temperatures are only adjustments at the used HGA, the real temperatures can be different so that for each particular instrument optimal conditions must be evaluated experimentally.

Reagents

Oxygen 99.9999%; Argon 99,999%;
2-propanol p.a.; Carbon tetrachloride p.a.;
The standard solutions (10 ng Cd^{2+}/ml in 2-propanol) were prepared each day from an aqueous stock solution (10 μg Cd^{2+}/ml in 0.1 M HNO_3) by successive dilution with 2-propanol.

Procedure

Fuels, oils with lower boiling points and crude oils: The oil samples were spiked with 0.3–0.6–0.9 ng Cd/ml oil by adding a measured volume of Cd-standard solution (10 ng Cd^{2+}/ml in 2-propanol). 20 μl were deposited directly on the platform with the autosampler.

Heavy fuel oil: The weighed oil samples ($\sim$2 g) were diluted with a defined amount of CCl_4 ($\sim$6 g) and suspended. Subsequently they were spiked with 0.20–0.4–0.6 ng Cd^{2+}/ml suspension by addition of a distinct volume of Cd-standard solution (10 ng Cd^{2+}/ml in 2-propanol). 10 μl were deposited directly on the platform with the autosampler.

2-propanol is used to rinse the tubings etc. of the autosampler. If necessary the temperature programme has to be optimized for each individual oil sample. Furthermore, the age dependent alteration of the tube and its influence on the true temperature must be considered.

RESULTS AND DISCUSSION

Oxygen ashing step

Experiments with oil samples and a temperature programme, normally applied for cadmium in aqueous solutions with argon as sheat gas, showed the uselessness of such a common procedure. At the atomization step there was still so much undigested residue on the platform that the compensation ability of the Zeeman-instrument was inadequate and therefore the cadmium peak was obscured by interference peaks. Hence it was necessary to improve the charring step as far as necessary to ash most of the interfering residue. Nitric acid was excluded, because it is not miscible with oil and moreover its cadmium blanks were too high compared to the extremely low cadmium contents in the materials investigated.

For better ashing in graphite furnaces it has been described that oxygen can be influxed into the internal gas flow of the graphite tube with maximal 300 ml/min during the drying- and charring step.[5,6] Therefore oxygen was chosen to obtain a satisfactory ashing of interfering residues. The choice of the temperature programme, however, is important to obtain optimal signals. Drying temperature and drying times are chosen in such a way, that the oil sample distills smoothly from the platform. For the charring step, the temperature must be optimized in such a manner that an optimal destruction of the matrix without cadmium losses can be achieved.

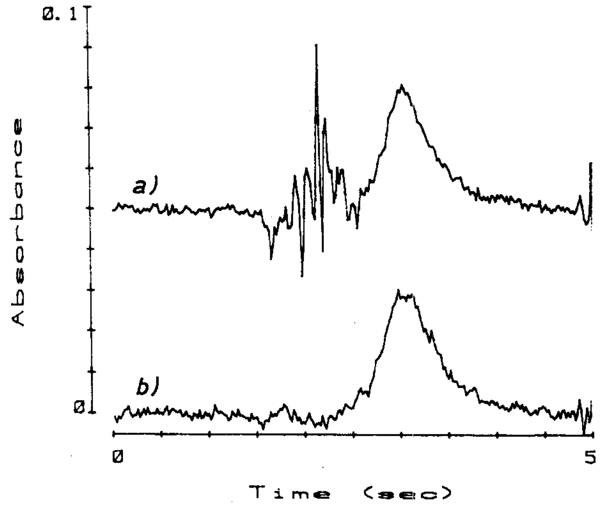

FIGURE 1 Direct determination of cadmium in crude oil. Cd-absorption peak dependent upon the charring temperature (a) 500°C (b) 530°C.

The influence of charring temperature on the cadmium absorption peak in crude oil samples is shown in Figure 1.

Moreover, the "ramp time" and the "hold time" during charring are of great importance. Rapid raising of the temperature results in an explosive combustion of the oil sample in the oxygen flow. Thus, for complete destruction of the matrix, a longer "hold time" of the ashing temperature is necessary, see Figure 2.

With oxygen, relatively high charring temperatures are obtained. It is evident that oxygen not only reacts as an oxidation reagent, but also as an element modifier. Thus, it prevents cadmium losses even at temperatures above 500°C, as shows a comparison between cadmium peaks in Nigeria crude oil with and without oxygen addition (Figure 3). An explanation for this effect may be the formation of an oxygen chemisorption layer on the graphite surface. This causes an alteration in the atomization mechanism.[7]

In addition to ashing, the atomization conditions are carefully investigated. A maximal heating rate yields interference peaks despite Zeeman compensation, whereas a heating rate with a ramp time of 1 sec. shows undisturbed cadmium peaks (Figure 4).

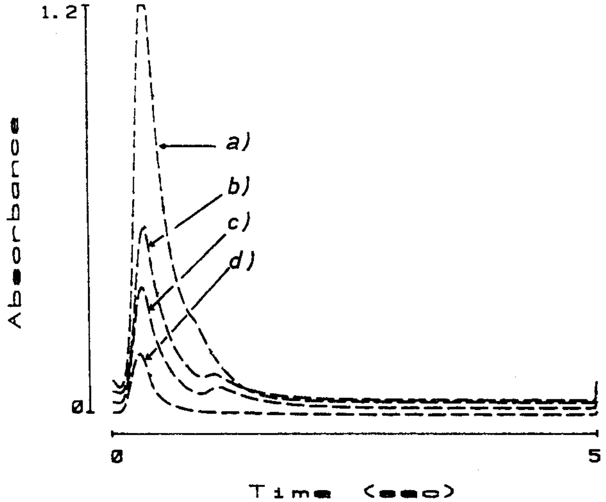

FIGURE 2 Direct determination of cadmium in light fuel oil. Background absorption dependent on charring time. (single beam mode)
a) 20 s at 400°C b) 80 s at 400°C
c) 100 s at 400°C d) 180 s at 400°C

The analytical life time of the pyro tubes is only insignificantly reduced despite the application of pure oxygen at temperatures around 500°C. It is comparable with the life times of tubes in which nitric acid solutions from wet digestion are injected. On average they can reach life times of about 400 firings.

Refined oils can be distilled from the platform without residue. Crude oils show a moderate formation of charcoal, however, it can easily be removed from the platform. An occlusion of cadmium in this residue during analyses can be excluded. Otherwise the regression line would show a systematic slope. Moreover, during a 10 fold repetition of the measurement with the same sample, the absorbance remained practically constant.

Consequently the application of oxygen during the drying and charring step represents an effective and elegant method, to diminish the background absorption from complex organic matrices, so that very small cadmium signals can be measured without problems.

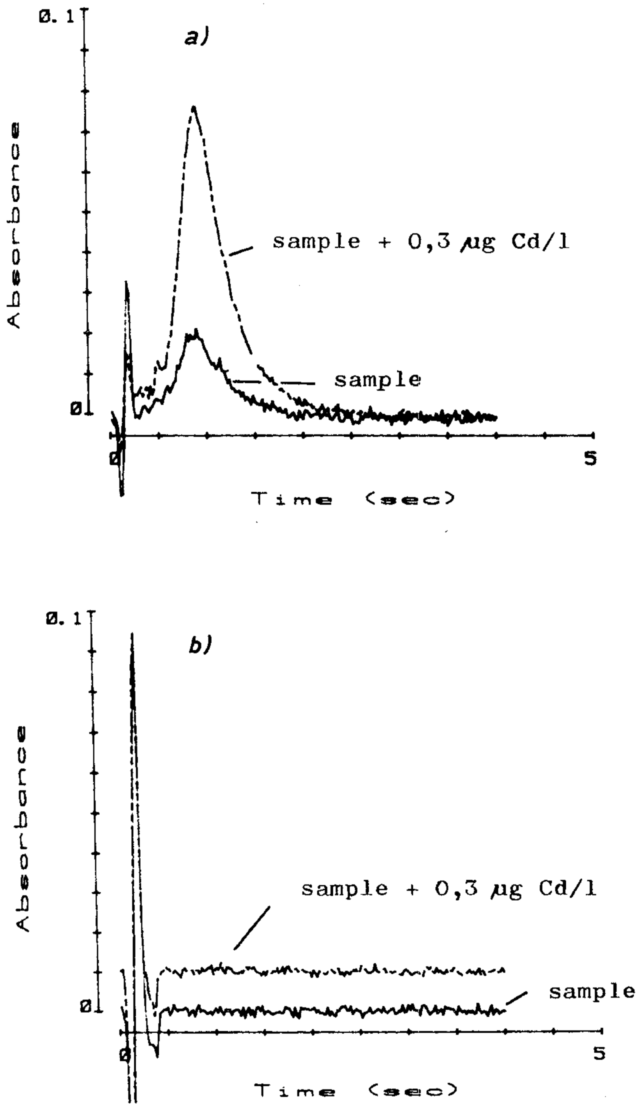

FIGURE 3 Direct determination of cadmium in crude oil. Effect of oxygen as element modifier.
Charring temperature: 530°C;
Atomization temperature: 1500°C
a) with oxygen b) without oxygen

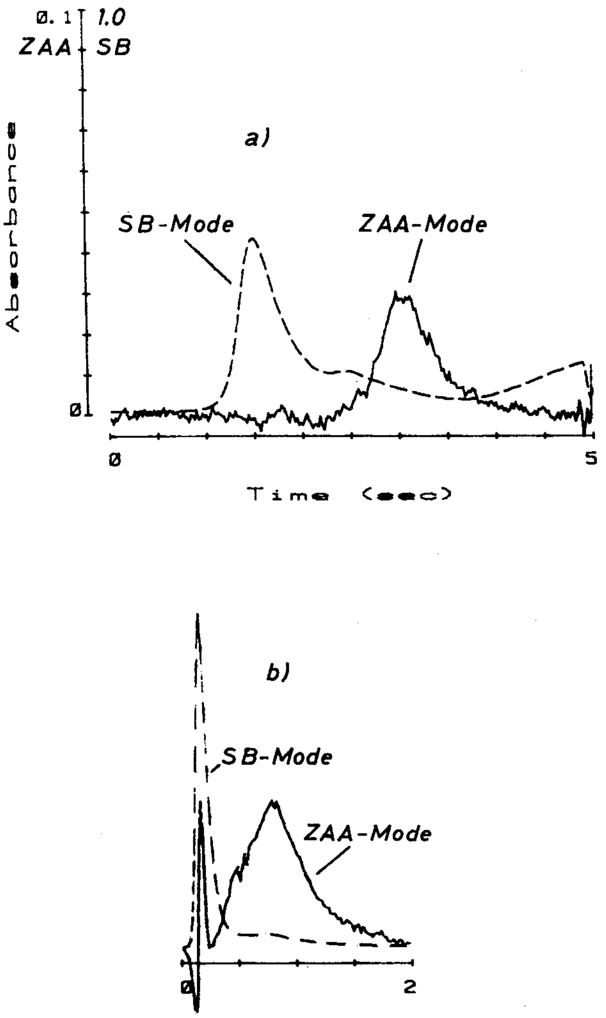

FIGURE 4 Direct determination of cadmium in crude oil. Influence of the atomization parameters on the cadmium peak.

a) 1900°C, 1 s ramp time.

b) 1500°C, 0 s ramp time.

PRECISION, ACCURACY, EVALUATION, DETECTION LIMIT

Precision

Repeated measurement (peak height evaluation) with a crude oil sample having a cadmium content of 0.3 μg/l gave the following standard deviations:

1) Day-to-day precision: $\pm 12.1\%$ ($n=3$)
2) Within-run precision: $\pm 5.8\%$ ($n=10$)

Accuracy

In order to prove the accuracy of the analytical results, some samples with higher cadmium content were analysed with two independent methods:

1) HNO_3—$HC10_4$ digestion; determination with differential pulse anodic stripping voltammetry (DPASV).[8]

2) Acid extraction (0.5 ml oil + 1 ml CCl_4 + 1 ml HNO_3 1:4 + 10 μl 10% Triton-X-100) followed by determination with graphite furnace atomic absorption spectrometry (GFAAS),[9] see Table II.

TABLE II
Accuracy checks for the direct determination of cadmium in crude oil and products (values in μg/l)

Sample	Direct determination with HGA 500	Acid-extraction determination with HGA 500	DPASV after wet digestion
Cd/2nd intercalibration exercise, sample 3	0.33	0.35	0.33
North Sea—crude oil	0.08	0.07	—
Nigeria—crude oil	0.17	0.14	—

Evaluation

Provided that interference peaks are absent, the evaluation by peak height and peak area shows good agreement, see Table III.

In addition, the crude oils are evaluated by the standard addition method as well as with the aid of a matrix matched calibration graph. The use of a matrix matched calibration graph means the

TABLE III
Cd contents in crude oils (μg/l). Comparison between peak height and peak area evaluation

Sample	Peak height	Park area
Cd/2nd DGMK intercalibration exercise, sample 3	0.37	0.37
Libyan—crude oil	0.064	0.075
Arabian light—crude oil	0.094	0.103
Nigeria—crude oil	0.163	0.163
North Sea—crude oil	0.076	0.076

regression line by obtained standard addition for another crude oil. The prerequisite for the application of this approach is that the regression line of the sample and the calibration graph have approximately the same slope. Table IV shows the cadmium content, obtained by both these evaluation methods, and the gradients of the regression lines by the standard addition method for the crude oil samples. Their standard deviation, i.e. maximal deviation, is ±11%. Since the cadmium contents are very low, this can be regarded as acceptable. The slope of the regression line for inorganic cadmium (Cd^{2+} in 2-propanol) shows that evaluation versus an aqueous cadmium standard solution using peak height is not possible. Due to

TABLE IV
Slopes of the calibration graphs and Cd contents of some crude oils. Evaluation by standard addition (peak height) and by a matrix matched calibration graph. (In the last column the matrix used as basis for the calibration graph is given).

Sample	Slope stand. add.	Cd-content (μg/l) peak height stand. add.	matrix matched calibration graph
Cd/2nd DGMK intercalibration exercise, sample 3	145.1	0.33	0.286 Arabian
Arabia—light—crude oil	151.4	0.085	0.094 Intercalibr.
Libya—crude oil	—	—	0.064 Intercalibr.
North Sea—crude oil	156.9	0.070	0.076 Nigerian
Nigeria—crude oil	121.3	0.165	0.171 North Sea
Cd^{2+} in i-propanol	83.8		

the necessary working conditions (see table II), evaluation by peak area versus an aqueous cadmium standard solution appears to be not achievable under the present but for reliable determinations unavoidable working conditions.

Detection limit

The detection limits are defined as three times the standard deviation of the electronic noise. This led to the following values: $<0.06\,\mu\text{g Cd/l}$ for crude oils and $<0.03\,\mu\text{g Cd/l}$ for fuel oils. For samples with less interfering matrix the detection limit can be lowered by multiple injections with intermediate drying. Therefore with three 20 µl injections each followed by a drying step the cadmium level can be estimated even in diesel fuel extremely low in cadmium (see Figure 5).

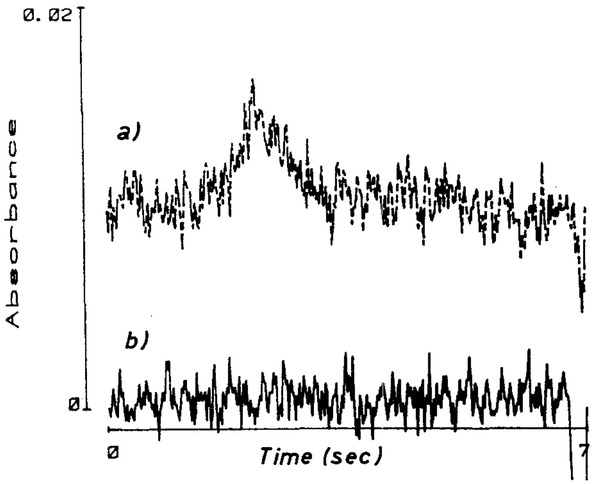

FIGURE 5 Direct determination of cadmium in Diesel fuel. (Content approx. 0.01 µg/1)
Application of multiple injections with intermediate drying.
a) 3 × 20 µl fuel
b) Firing without sample (instrumental noise)

ANALYTICAL RESULTS

In Table V the cadmium contents of various hitherto analyzed oil- and fuel samples are listed. The distilled products (fuels and light fuel oil) have extremely low cadmium contents ($<0.03\,\mu g$ Cd/l). In crude oils values are somewhat higher (0.06–0.17 μg Cd/l), whereas in the high boiling, viscous heavy fuel oils with contents around 1 μg Cd/l the highest values occur. In general the cadmium values found are well below formerly reported cadmium contents for similar materials.[2,10] This demonstrates the superiority of a direct determination in comparison to formerly used analytical methods which required severe contamination precautions and time consuming digestion procedures.

TABLE V
Cd—contents in crude oil and products

Sample	Cd—content
Fuels	
Carburetor fuel (CF)	$<0.03\,\mu g$ Cd/l
CF, tank 10509 (August 1982)	$<0.03\,\mu g$ Cd/l
CF, tank 505 (November 1982)	$<0.03\,\mu g$ Cd/l
Diesel fuel (DF)	$<0.03\,\mu g$ Cd/l
DF, tank 517 (August 1982)	$<0.03\,\mu g$ Cd/l
DF, tank 517 (November 1982)	$<0.03\,\mu g$ Cd/l
Crude Oils	
2nd intercalibration, sample 3	0.33 μg Cd/l
North Sea—crude oil	0.08 μg Cd/l
Libya—crude oil	0.06 μg Cd/l
Arabia—light—crude oil	0.09 μg Cd/l
Nigeria—crude oil	0.17 μg Cd/l
Fuel Oils (FOL)	
Fuel oil, light, coloured (FOL)	$<0.03\,\mu g$ Cd/l
FOL, tank 522 (August 1982)	$<0.03\,\mu g$ Cd/l
FOL, tank 522 (November 1982)	$<0.03\,\mu g$ Cd/l
Fuel oil, heavy (FOH)	0.80 μg Cd/kg
FOH, BC, tank 563 (September 1982)	0.99 μg Cd/kg
2nd intercalibration exercise, sample 4	0.95 μg Cd/kg

Note: Since after multiple injections of diesel fuel approximately 0.01 μg/l cadmium have been found it can be concluded that true cadmium contents in carburetor and diesel fuels probably are around this value.

From these data a preliminary calculation was made of the cadmium amount which could be released from crude oils and oil products in the Federal Republic of Germany. In the Federal Republic of Germany approximately 80,000,000 metric tons of mineral oil were consumed in 1982.[11] With an average cadmium content of about 0.1 μg Cd/l (crude oil) the highest released cadmium amount is only about 8 kg per year. Hence, the cadmium contamination of the environment caused by combustion of oil and oil products can be neglected, in comparison to the overall cadmium emissions from other sources into the atmosphere estimated to be approximately 60–80 t annually for the Federal Republic of Germany.[2,3]

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