DETERMINATION OF CADMIUM BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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In the presence of organic compounds, such as EDTA, citric acid or triethanolamine, the absorbance signal of Cd during atomization in a tube of electrographite or covered with pyrolytic graphite appears at a lower temperature than the signal from $CdCl_2$. Some of these compounds, e.g. EDTA, eliminate the interfering effect of NaCl and $MgCl_2$. With urine, however, addition of these compounds often causes splitting of the single absorbance pulse of Cd or an increase of one of the components of a splitted pulse. Addition of a simple modifier HNO_3 is therefore recommended for analyses of urine using atomization in a tube of electrographite. The evaluation of the cadmium concentration was done from integrated absorbances by the method of standard additions.

Of the elements determined by atomic absorption spectroscopy, cadmium has the lowest atomization temperature besides mercury. The temperature at which the Cd signal appears can change from 430°C in pure argon atmosphere to 870°C in an atmosphere of argon with 1% oxygen[1]. The mechanism of atomization varies according to the form in which Cd is present in the sample. Decomposition of nitrate and sulphate leads to CdO, atomization then proceeds by the reduction with graphite to the metal and by its evaporation, or thermal dissociation of the oxide[2−6]. Chloride atomizes either by dissociation or via oxide formation[2,5,6]. Some organic compounds (EDTA) cause an enhancement of Cd atomization and a shift of its signal to lower temperatures[7]. The latter effect is conditioned by the reaction between the oxide and carbon. The excess of carbon after decomposition of the reagent influences changes in the evaporation mechanism. The partial pressure of carbon in the gas phase increases by the addition of organic compounds. The influence of gaseous carbon was proved by changes of the Cd signal during separate additions of Cd^{2+} and EDTA onto various places in the tube or simultaneously on the tube wall and platform[7]. Carbonaceous residues after carbonization of organic compounds can increase the number of active sites in the graphite tube influencing the atomization of cadmium[8]. Organic compounds are also used as matrix modifiers for elimination of interfering effects during determination of cadmium[9].

The present work deals with a comparison of organic and inorganic matrix modifiers acting on Cd atomization from the wall of a graphite tube with regard to its determination in clinical material.

EXPERIMENTAL

Solutions and Apparatus

Standard solutions of $CdCl_2$ and $Cd(NO_3)_2$ were prepared by dissolving $CdCl_2.2\cdot5\,H_2O$ in $0\cdot1\,mol\,l^{-1}$ HCl and $Cd(NO_3)_2.4\,H_2O$ in $0\cdot1\,mol\,l^{-1}\,HNO_3$. The solutions were standardized complexometrically with xylenol orange as indicator; they contained $1\cdot01\,g\,l^{-1}Cd^{2+}$ and $0\cdot98\,g.\,l^{-1}\,Cd^{2+}$ All chemicals were of analytical purity grade.

Measurements were carried out on a Perkin–Elmer 3030 type atomic absorption spectrometer connected with a HGA-400 graphite furnace. The $228\cdot8$ nm resonance line was generated by a Perkin–Elmer electrodeless discharge lamp with 4 W input power and the transmitted spectral interval was $0\cdot7$ nm. Deuterium background correction was used to eliminate non-selective absorption. Data about height (A) and area $(A\,s)$ of absorbance peaks were evaluated. An automatic sampler AS-1 was used to inject 20 µl sample portions. Both, tubes of electrographite and those being covered in situ[10] with pyrolytic graphite were used. The graphite was also covered with a layer of Ta or Nb carbide by injection 50 µl of a 1% aqueous suspension of Ta_2O_5 or Nb_2O_5 into the tube and burning out, which procedure was repeated fifteen times. The suspension was first dried for 30 s at 150°C, then decomposed for 20 s at 800°C and for 5 s at 2 600°C; the ramp time of the temperature was 5 s and the flow rate of argon was 300 ml min^{-1}.

Photographs of organic reagent samples on graphite platforms after decomposition in the graphite tube were made with a Philips SEM 505 scanning electron microscope The graphite platforms were prepared by cutting the graphite tube longitudinally into four parts. The platform was placed in a tube, wetted with 10 µl of a 1% solution of the reagent, dried for 25 s at the tube wall temperature 300°C (ramp time of 15 s) and the sample eventually decomposed for 20 s at the tube wall temperature 1 000°C (ramp time of 5 s). The platform was removed from the tube after cooling.

TABLE I

Temperature regime for the analysis of urine

	$T,\,^\circ C$	t_R, s	Hold, s
Drying	140	30	20
Decomposition	380	30	15
Atomization[a]	1 500	1	4
Cleaning	2 500	3	2

[a] Rate of flow of argon 50 ml min^{-1}.

The Cd concentration causing $A = 0.0044$ after applying 20 µl of the sample is characteristic for the actual sensitivity. The relative standard deviation was calculated from five independent measurements. The detection limit is the Cd concentration causing $A = \bar{A}_0 + 3s_0$, where $\bar{A}_0$ is the mean blank absorbance and s_0 its standard deviation (from 6 measurements).

Method of Determination of Cd in Urine

An amount of 20 µl of urine diluted 1 : 1 with 0.03 mol l^{-1} HNO$_3$ was injected into the electro-graphite tube and treated according to Table I. The concentration of Cd was determined by the standard addition method if the integrated absorbance was evaluated. The recovery of the addition of 0.5—3 µg l^{-1} Cd^{2+} was 97—101%. The relative standard deviation of the determination of 0.82 µg l^{-1} Cd was 3.8%. The calibration curve was linear up to 5 µg l^{-1} Cd. The characteristic concentration was 0.081 µg l^{-1} Cd and the detection limit was 0.045 µg l^{-1} Cd.

RESULTS AND DISCUSSION

Atomization from CdCl$_2$ and Cd(NO$_3$)$_2$

Evaluation results of the decomposition and atomization curves are given in **Table II**. The highest possible decomposition temperature at which no loss of cadmium occured was estimated on the basis of the constant integrated absorbance. The

TABLE II

Decomposition and atomization temperatures and optimum conditions for the determination of cadmium

Properties	Limiting conditions[a,b], °C		Optimum conditions		
	electrographite	pyrographite	T, °C	t_R, s	hold, s
Drying	—	—	150	5[g], 15[h]	25[g], 15[h]
Decomposition	650[a,d], 700[a,e]	500[a,d,e]	300	5	15
Atomization	1 650[b,d], 1 700[b,e] 900[c]	1 450[b,d], 1 500[b,e]	2 000[f]	3	2
Cleaning	—	—	2 500	3	2

[a] Highest usable decomposition temperature without loss of the signal A s; [b] lowest atomization temperature for attaining the maximum of the signal A s for the temperature ramp time $t_R = 1$ or 3 s; [c] lowest atomization temperature for attaining maximum height of the absorbance peak at the temperature ramp time $t_R \approx 0$; [d] CdCl$_2$; [e] Cd(NO$_3$)$_2$; [f] rate of flow of argon 50 ml min^{-1}; [g] electrographite; [h] pyrolytic graphite.

dependence of the peak height on the decomposition temperature was constant for lower temperatures, e.g. up to 250°C for $CdCl_2$ on pyrolytic graphite. The atomization curve attained for a temperature ramp time $t_R = 1$ or 3 s a constant signal value earlier for the integrated absorbance than for the peak height absorbance evaluation. At the most rapid, controlled temperature ramp $(t_R \approx 0)$, a constant absorbance was attained at atomization temperatures $\geqq 900$°C, but the integrated absorbance began to decrease moderately from 800°C.

The relative standard deviation for the determination from $CdCl_2$ at a concentration of 1 µg l^{-1} Cd on electrographite was 1·2% for $t_R = 3$ s, 5·1% for $t_R \approx 0$ at the argon flow rate of 50 ml min^{-1}, and 3·8% for $t_R = 3$ s at stopped flow of argon. Optimum conditions for pure Cd^{2+} solutions are given in Table II. At stopped flow of argon, the signals of Cd from $Cd(NO_3)_2$ in the presence of 0·01 mol l^{-1} HNO_3 were higher (by 20% in peak height, by 40% in peak area) than from $CdCl_2$ in 0·01 mol l^{-1} HCl. The same signals were obtained at argon flow rate of 50 ml min^{-1}. Under optimum conditions the relative standard deviations were 1·2% from $CdCl_2$ or 2·7% from $Cd(NO_3)_2$ (electrographite) and 3% from $CdCl_2$ or 6·7% from $Cd(NO_3)_2$ (pyrolytic graphite). The relative standard deviation dropped to one half after about 100 firings of a new tube with a pyrolytic graphite layer. With a new tube coated with pyrolytic graphite, the peak height absorbance dropped to the value obtained on electrographite after about 100 firing cycles (drying, decomposition, atomization). Thus, the results done from measurements of the peak height depend considerably on the state or previous use of the graphite. On the contrary, the signal area did not change with the time and was the same as with a tube of electrographite. The signals discussed in the present work in connection with pyrographite were always obtained on a used tube coated with a pyrolytic layer.

A higher reproducibility was attained for $CdCl_2$ in 0·01 mol l^{-1} HCl. The calibration curve was linear for a tube coated with a pyrolytic layer up to 2 µg l^{-1} Cd, for a tube of electrographite up to 4 µg l^{-1} Cd if peak heights were evaluated, and up to 6 µg l^{-1} Cd for both graphite types based on the peak area evaluation. The signal obtained on pyrolytic graphite was splitted at $\varrho_{Cd} > 2$ µg l^{-1}; the first part of the pulse probably corresponded to the atomization coming from $CdCl_2$ and the second to the atomization via CdO. No splitting of the signal was observed on electrographite. The characteristic concentration was equal to 0·055 µg l^{-1} Cd and the detection limit was 0·071 µg l^{-1} Cd.

Influence of Inorganic Acids

The influence of acids on the decomposition and atomization is illustrated in Table III. The height and area of the peak for Cd did not depend on the HCl concentration up to 2 mol l^{-1}, but both quantities increased with the HNO_3 concentration up to 0·3 mol l^{-1}, at which the peak height on pyrolytic graphite increased by 50% and

the area by 70%. No such effect was observed on electrographite. Nitric acid caused a shift of the pulse toward higher temperatures on both graphite kinds (Fig. 1).

Addition of sulphuric acid caused lower reproducibility; when its concentration exceeded $0.2 \text{ mol } l^{-1}$, a non-selective signal appeared prior to the selective Cd signal. This effect was eliminated by increasing the decomposition temperature above $390°C$.

TABLE III

Recommended temperatures for decomposition and those for the beginning of atomization in the presence of inorganic acids ($0.5 \text{ mol } l^{-1}$)

Acid	$T_d, °C^a$		$T_a, °C^b$	
	pyrographite	electrographite	pyrographite	electrographite
$—^c$	500	650	900	1 150
HCl	500	650	1 350	1 350
HNO_3	700	900	1 400	1 400
H_2SO_4	500	800	1 000	1 400
H_3PO_4	850	1 000	1 500	1 600

^{a} Highest usable decomposition temperature; ^{b} temperature at which the Cd signal runs on for measurement of the atomization curve at $t_R = 3 \text{ s}$; ^{c} $1 \text{ μg } l^{-1}$ Cd^{2+} in $0.01 \text{ mol } l^{-1}$ HCl.
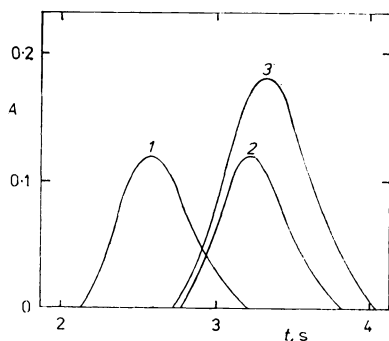

FIG. 1

Influence of $0.3 \text{ mol } l^{-1} HNO_3$ on the signal of Cd ($1 \text{ μg } l^{-1}$). Medium: *1* sole $CdCl_2$, electrographite; *2* HNO_3, electrographite; *3* HNO_3, pyrolytic graphite
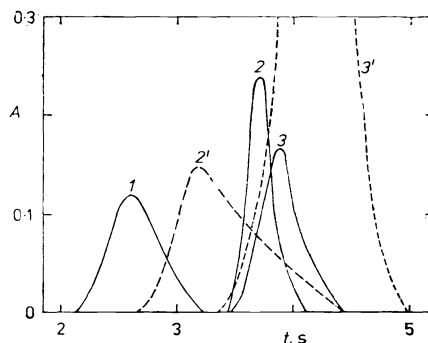

FIG. 2

Influence of $0.3 \text{ mol } l^{-1}$ H_3PO_4 on the signal of Cd ($1 \text{ μg } l^{-1}$). Medium: *1* sole $CdCl_2$, electrographite; *2* H_3PO_4, pyrolytic graphite; *2′* as *2*, background; *3* H_3PO_4, electrographite; *3′* as *3*, background

Phosphoric acid caused a shift of the Cd absorbance signal toward higher atomization temperatures (Fig. 2). When its concentration was 0.1 mol l^{-1}, the absorbance on electrographite increased by 40% and that on pyrolytic graphite by as much as 100%. For more than 0.1 mol l^{-1}, the Cd signal on electrographite remained the same, that on pyrolytic graphite decreases a little. The peak area was constant up to a concentration of 0.3 mol l^{-1} H$_3$PO$_4$; at a concentration of 2 mol l^{-1} on pyrographite the area increased by about 18%, that on electrographite decreased by 18%. In the presence of H$_3$PO$_4$ the signal on electrographite did not change for the temperature ramp time decreasing from 3 s to 0. The signal due to non-selective absorption increased with the concentration of H$_3$PO$_4$ from 0.15 mol l^{-1} on both graphite types. On electrographite, the background signal overlapped with the Cd signal; on pyrolytic graphite these signals were better separated (Fig. 2). A suitable concentration of H$_3$PO$_4$ was 0.1 mol l^{-1}.

Influence of NaCl *and* MgCl$_2$

Sodium chloride caused a marked irreproducibility of the measurements. Beginning from a concentration of 2 g l^{-1} NaCl, the Cd signal was splitted into two ill-reproducible parts (Fig. 3) and it was not possible to measure its height; moreover the absorbance pulse was shifted to higher temperatures. The highest decomposition temperature for Cd in the presence of 0.5 mol l^{-1} NaCl was 500°C on pyrographite or 550°C on electrographite, respectively. When the maximum of the second part
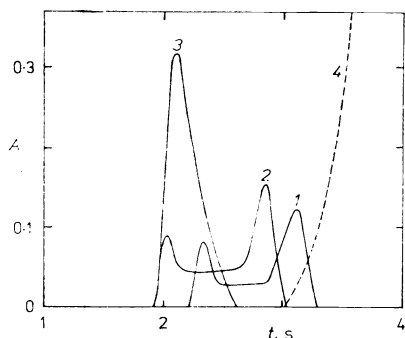

Fig. 3

Signal of Cd (1 μg l^{-1}) in the presence of NaCl (10 g l^{-1}) and EDTA (1 g l^{-1}). Medium: *1* NaCl, pyrolytic graphite; *2* NaCl + EDTA, pyrolytic graphite *3* NaCl + EDTA, electrographite; *4* background on both graphite kinds, NaCl or NaCl+ EDTA
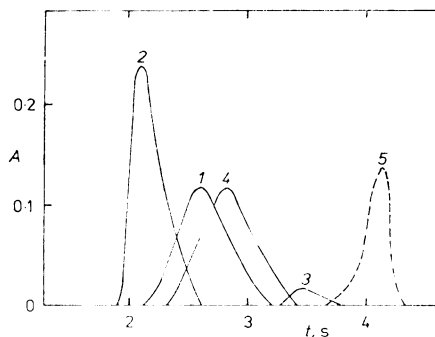

Fig. 4

Signal of Cd (1 μg l^{-1}) in the presence of MgCl$_2$ (10 g l^{-1}) and EDTA (1 g l^{-1}) in an electrographite tube. Medium: *1* sole CdCl$_2$; *2* EDTA; *3* MgCl$_2$; *4* MgCl$_2$ + EDTA; *5* background, MgCl$_2$ and MgCl$_2$ + EDTA

of the Cd pulse was attained, the background signal appeared at a concentration of NaCl 0.1 g l^{-1} and more. Partial overlapping of the selective and non-selective signals for concentrations of NaCl above 3 g l^{-1} requires an evaluation of the fore part of the Cd pulse. In the presence of NaCl up to a concentration of 10 g l^{-1}, the Cd signal on pyrographite varied between $80-100\%$, on electrographite between $90-100\%$ with respect to the $CdCl_2$ standard signal. At $t_R \approx 0$ and atomization temperature of $900°C$, the non-selective absorbance on both graphite kinds was lower and better separated from the Cd pulse than at $t_R = 3$ s, but the relative standard deviation was 40%.

Magnesium chloride lowered the Cd signal on both graphite kinds by 75% beginning from a concentration of 1 g l^{-1}, but no splitting of the signal took place. A non-selective signal appeared at a concentration of $MgCl_2$ of 4 g l^{-1} but could be eliminated by a deuterium correction of the background (Fig. 4).

Influence of Organic Reagents

EDTA, ascorbic acid and glucose increase the absorbance of Cd till a concentration of 0.5 g l^{-1} above which the absorbance being constant up to 10 g l^{-1}. For concentrations of ascorbic acid above 2 g l^{-1} the signal dropped slightly. The concentration of 1 g l^{-1} was chosen as optimal for all reagents.

The highest practical decomposition temperatures in the presence of the organic reagents on electrographite as on pyrolytic graphite were identical in the range $300-400°C$ except of tiron and thiourea, for which the temperature was $500°C$. The atomization signal for Cd ran on in the range $600-750°C$, or with thiourea at $800°C$ or with tiron at $1\,000°C$ respectively as determined from atomization curves at $t_R = 3$ s. Thus, the Cd signal in the presence of most organic reagents appeared earlier than from pure $CdCl_2$.

Concerning the time, the absorbance pulses, were shifted in the presence of EDTA (Fig. 5), citric acid and triethanolamine. Except of tiron (Fig. 5), the Cd pulses were
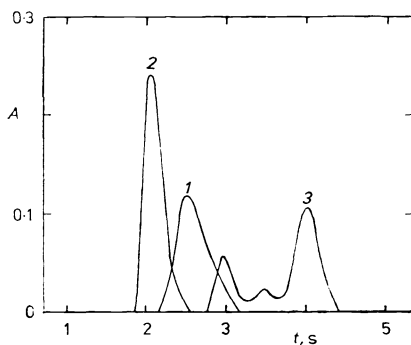

Fig. 5

Influence of EDTA and tiron (1 g l^{-1}) on the signal of Cd (1 µg l^{-1}) in a tube coated with pyrolytic graphite Medium: *1* sole $CdCl_2$; *2* EDTA; *3* tiron

not splitted. In the presence of ascorbic acid, the relative standard deviation was 3.5% for 1 µg l^{-1} Cd at $t_R \approx 0$, or 0.4% at $t_R = 3$ s. The effect of organic reagents on the height and area of the Cd signal is summarized in Table IV. EDTA appears the best on both graphite kinds. In the presence of 1 g l^{-1} EDTA the calibration curve was linear up to 5 µg l^{-1}, the characteristic concentration was 0.024 µg l^{-1}, and the detection limit was 0.031 µg l^{-1} Cd. The relative standard deviation for 1 µg l^{-1} Cd was 0.9%.

The location of the sample on the graphite surface was followed by electron scanning microscopy. After drying the EDTA solution, small crystals remained on the pyrolytic graphite surface, whose number was lower when a higher temperature was used (Figs 6 and 7). In the presence of 100 µg of ascorbic acid, a melt resulted on the surface of the pyrolytic graphite after heating (temperature of the tube wall was 1 000°C). On electrographite, the crystals of the reagent were not distinguishable from the graphite structure. The location of the sample on the surface of the atomizer is one of the factors influencing the absorbance signal[7]. For example, ascorbic acid or sacharose hindered the diffusion of analyte (zinc) into the boundary regions of the atomizer[11].

Suppression of the Interference of NaCl *and* MgCl$_2$ *by Adding Modifiers*

Organic reagents decreased the atomization temperature of Cd in the presence of NaCl. However, the signal on pyrographite remained splitted for all reagents. Differences among modifiers were observed on electrographite, since EDTA (Fig. 3), ascorbic acid, lactic acid, glucose, glycocoll and triethanolamine gave rise to a non--splitted pulse, sufficiently separated from the signal of the background. With other reagents, the signal was splitted similarly as on pyrolytic graphite. EDTA, ascorbic acid and glucose increased the peak area approximately by 40% compared to the signal area from CdCl$_2$. Other reagents had no influence. Sufficient separation of the selective and non-selective signals and a non-splitted signal during atomization from electrographite with additions of EDTA, glucose and ascorbic acid allowed the determination of Cd even in the presence of 10 g l^{-1} NaCl. Splitted pulses were obtained for Cd in the presence of MgCl$_2$ and organic reagents, but they were non-splitted on both kinds of graphite tubes with EDTA (Fig. 4) and triethanolamine. In the presence of thiourea, tiron and acetic acid the non-selective signal partly overlapped with the Cd signal. The effect of MgCl$_2$ after the addition of organic reagents is illustrated in Table IV. Optimal is the addition of EDTA or triethanolamine. The decrease of the atomization temperature of cadmium by organic reagents causes more efficient separation of analyte from the non-volatile matrix of the sample, but these reagents can affect the crystal structure of the matrix. In such case, certain organic reagents that do not facilitate the atomization of cadmium from pure solutions can act as matrix modifiers, as e.g. histidine in the determination of cadmium in sea water[12].

The cadmium signal on both, electrographite and pyrolytic graphite remained splitted in the presence of NaCl and 0.3 mol 1^{-1} HNO_3. However, the non-selective signal could be removed by the deuterium correction of the background even in the

FIG. 6
SEM photograph of a pyrolytic layer with 100 µg of EDTA (after drying at tube wall temperature of 300°C). Magnification 1 010×
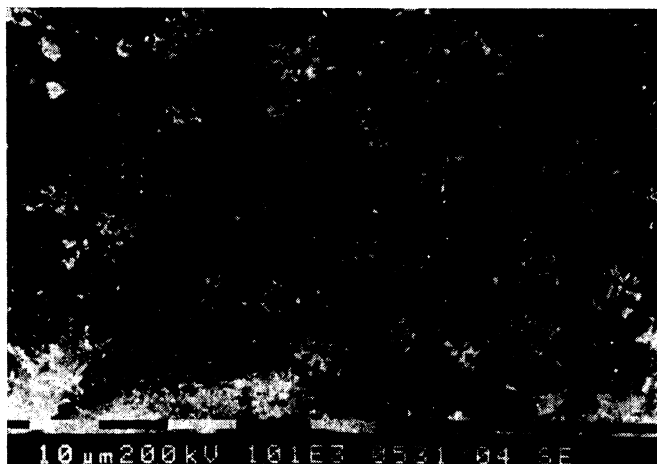

FIG. 7
SEM photograph of a pyrolytic layer (used) with 100 µg of EDTA (after decomposition at tube wall temperature of 1 000°C). Magnification 1 010×

presence of 10 g l^{-1} NaCl. The background was lower on electrographite than on pyrolytic graphite. The height of the frontal part of the pulse grew with the concentration of NaCl. The signal was not splitted by HNO_3 in the presence of $MgCl_2$. The maximum decomposition temperature on pyrographite was 450°C, on electrographite 800°C. The influence of HNO_3 on the signal in the presence of NaCl and $MgCl_2$ is illustrated in Table V. Nitric acid ensures a changeless signal area in the presence of NaCl and $MgCl_2$ when electrographite is used. In spite of splitting of the signal in the presence of NaCl, it is possible to use HNO_3 for the atomization on electrographite and measurement of the integrated absorbance.

The highest decomposition temperature in the presence of $MgCl_2$ and H_3PO_4 was 1 000°C on both graphite kinds. The interfering influence of $MgCl_2$ on the peak height on pyrolytic graphite was partially suppressed by $0.1 \text{ mol l}^{-1} H_3PO_4$, whereas the suppression was complete up to $4 \text{ g l}^{-1} MgCl_2$ when the peak area was evaluated (Table V), for higher concentrations, the peak area still increased. On electrographite H_3PO_4 suppressed the influence of $MgCl_2$ entirely regardless of whether the height

TABLE IV

Influence of organic reagents on the signal of cadmium

Reagent	I^a				II^a			
	$A_{rel}{}^b$		$(A s)_{rel}{}^b$		$A_{rel}{}^b$		$(A s)_{rel}{}^b$	
	E^c	P^c	E^c	P^c	E^c	P^c	E^c	P^c
—	1·0	1·0	1·0	1·0	0·2	0·2	0·2	0·2
EDTA	2·0	2·0	1·2	1·2	1·0	1·3	1·2	1·2
Glucose	1·7	1·7	1·5	1·3	1·2	1·2	1·2	1·2
Ascorbic acid	1·4	1·4	1·1	1·5	0·5	0·7	0·6	1·1
Citric acid	1·4	1·4	1·1	1·1	0·9	1·1	1·0	1·2
Acetic acid	1·3	1·3	1·0	0·8	0·3	0·2	0·2	0·2
Lactic acid	1·0	1·0	1·0	0·6	1·2	0·8	1·1	1·2
Tartaric acid	0·8	1·2	1·0	1·0	0·7	1·2	0·7	0·7
Triethanolamine	1·0	1·0	0·9	0·5	1·1	1·4	1·2	1·2
Thiourea	0·6	1·0	1·0	0·9	0·3	0·1	0·3	0·1
Tiron	0·9	0·9	1·1	1·0	0·5	0·3	0·6	0·4
Glycocoll	0·8	0·8	0·9	0·7	0·8	1·2	0·8	1·0
Oxalic acid	0·7	0·7	0·9	1·0	0·4	0·4	0·2	0·1

[a] I In the presence of 1 g l^{-1} reagent, II in the presence of $10 \text{ g l}^{-1} MgCl_2$ and 1 g l^{-1} reagent; [b] $A_{rel} = A_x/A_0$, $(A s)_{rel} = (A s)_x/(A s)_0$, where A_x and $(A s)_x$ denote the signals in the presence of the reagent and reagent with $MgCl_2$, respectively, A_0 and $(A s)_0$ denote the signals of 1 μg l^{-1} . Cd^{2+} (in the form of $CdCl_2$); [c] E means electrographite, pyrolytic graphite.

or the area of the peaks was evaluated. Non-selective absorption caused by $MgCl_2$ appeared together with the Cd peak at concentrations of $MgCl_2 \geqq 2$ g l^{-1}.

In the presence of 5 g l^{-1} $NH_4H_2PO_4$, the highest usable decomposition temperature on pyrographite was shifted to 850°C and the absorbance peak of Cd was higher by a factor of 2·5 compared to the pure $CdCl_2$ solution; on electrographite the corresponding values were 950°C and 1·5. However, the interfering influence of 10 g l^{-1} NaCl was not eliminated by the mentioned amount of phosphate. When the latter was in approximately equimolar concentration, 20 g l^{-1}, the decomposition temperature was shifted to 1 000°C on pyrolytic graphite, while one lectrographite it remained at 950°C, and the absorbance peak increased (Table V). By using a mixture of 10 g l^{-1} NH_4NO_3 and 20 g l^{-1} $NH_4H_2PO_4$ the same peak area was attained as from $CdCl_2$, but the selective and non-selective signals were not separated. In the presence of $NH_4H_2PO_4$ and NaCl or $MgCl_2$ the decomposition temperature 1 100°C could be used. The influence of $MgCl_2$ was suppressed when either the height or the area of the peak on electrographite was measured, or when the peak area was measured on pyrographite. Non-selective absorption increased beginning from 2 g l^{-1} $MgCl_2$.

TABLE V

Influence of HNO_3, H_3PO_4 and $NH_4H_2PO_4$ on the determination of Cd in the presence of $MgCl_2$ and NaCl

Addition	A_{rel}[a]		$(A\,s)_{rel}$[a]	
	E[b]	P[b]	E[b]	P[b]
—	1·0	1·0	1·0	1·0
HNO_3[c]	1·0	1·5	1·0	1·6
HNO_3[c] + $MgCl_2$[d]	0·7	0·2	1·0	0·7
$MgCl_2$[e]	0·2	0·2	0·2	0·2
HNO_3[c] + NaCl[d]	—	—	1·0	0·8
H_3PO_4[f]	1·4	2·0	1·0	1·0
H_3PO_4[f] + $MgCl_2$[e]	1·4	1·3	1·0	1·5
$NH_4H_2PO_4$[g]	2·5	5·7	1·6	1·8
$NH_4H_2PO_4$[g] + $MgCl_2$[d]	2·5	2·1	1·6	1·8
$NH_4H_2PO_4$[g] + NaCl[d]	1·5	1·5	1·1	1·5
$NH_4H_2PO_4$[g] + NH_4NO_3[e] + NaCl[d]	1·5	2·4	1·0	1·0

[a] $A_{rel} = A_x/A_0$, $(A\,s)_{rel} = (A\,s)_x/(A\,s)_0$, where A_x and $(A\,s)_x$ denote the signals of the analyzed solution and A_0, $(A\,s)_0$ those of the standard solution of 1 µg l^{-1} Cd^{2+} on the given surface; [b] E means electrographite, P pyrographite; [c] 0·3 mol l^{-1}; [d] 5 g l^{-1}; [e] 10 g l^{-1}; [f] 0·1 mol l^{-1}; [g] 20 g l^{-1}.

Atomization from Graphite Tubes Coated with Ta and Nb Carbides

For both surfaces, the highest decomposition temperature was 650°C and the lowest atomization temperature 1 800°C at $t_R = 3$ s. The height of the signal was larger by the factor of 1·4 on Ta carbide and its area was the same as on electrographite. On Nb carbide, no changes of Cd peak height and area were observed in comparison with electrographite. The calibration curves from peak height absorbance were linear up to 3·5 µg l^{-1} Cd or 6 µg l^{-1} Cd respectively if the integrated absorbance was evaluated. The characteristic concentration on Ta carbide was 0·038 µg l^{-1} and the detection limit was 0·045 µg l^{-1} Cd. The relative standard deviation for 1 µg . l^{-1} Cd was 2·4% on Ta carbide and 3·2% on Nb carbide.

Metal carbides disturb the structure of upper graphite layers and thus prevent the formation of lamellar compounds which would retain the matrix, e.g. metal chlorides[13,14]. Addition of NaCl did not cause splitting of the signal and a shift of the peak when carbides were used for graphite surface modifications. The relative standard deviation was, however, 30% for evaluation of the peak heights and 35% for the peak areas. By HNO$_3$ the Cd signal was splitted in the presence of NaCl, but the peak area was the same as without NaCl. The relative standard deviation for the determination of 1 µg l^{-1} Cd in the presence of $0 - 10$ g l^{-1} NaCl and 0·3 mol . . l^{-1} HNO$_3$ was 2·8% on the Ta carbide and 8·4% on Nb carbide when the peak area was measured.

On Ta carbide, the height as well as the peak area of the Cd signal decreased up to the concentration of 5 g l^{-1} MgCl$_2$, then the absorbance remained constant but only one half of the value of the pure CdCl$_2$ signal. A non-selective signal appeared for 4 g l^{-1} MgCl$_2$. Neither the peak height nor the area was observed to decrease on niobium carbide. The background signal appeared only for MgCl$_2$ concentrations $\geqq 10$ g l^{-1}.

Analysis of Urine

The samples were measured under the temperature regime indicated in Table I. The results varied according to the composition of the matrix of the samples. The Cd signals were both uniform and splitted. The height and form of the background signal with two marked peaks changed also considerably (the height of the background absorbance peaks varied from 0·030 to 0·700). The scatter of literature data can be explained by the variability of the matrix. The modifiers proposed in the literature were tested in the temperature regime of the present work, namely NH$_4$H$_2$PO$_4$ + HNO$_3$ (ref.[15]), NH$_4$NO$_3$ + NH$_4$H$_2$PO$_4$ + HNO$_3$ + TRITON X-100 (ref.[16]), and HNO$_3$ (ref.[17]) on both, electrographite and pyrolytic graphite. The latter was used preferably with the mixture containing phosphate, whereas 0·01 mol l^{-1} HNO$_3$ gave better results on electrographite. With the modifier 0·01 mol l^{-1} NH$_4$H$_2$PO$_4$ + 0·8 mol l^{-1} HNO$_3$, the relative standard deviation was

13·6% and the recovery of Cd^{2+} was 90%. With $0·06 \text{ mol } l^{-1} \text{ NH}_4\text{NO}_3$ + $0·013 \text{ mol } l^{-1} \text{ NH}_4\text{H}_2\text{PO}_4 + 0·16 \text{ mol } l^{-1} \text{ HNO}_3 + 0·01\% \text{ TRITON X-100}$ they were 21% and 68%, and with $0·01 \text{ mol } l^{-1} \text{ HNO}_3$ 12% and 78% (relative standard deviation and recovery). The results of analyses agreed in some cases only. The data were obtained by evaluating the peak heights; when the peak areas were measured, the results obtained with phosphate-containing modifiers were still worse. Much better results were obtained when HNO_3 was used and peak areas were evaluated. The relative standard deviation was 4−7% and the recovery of Cd approached 100%.

In addition to the mentioned modifiers, we tried to apply EDTA, glucose, and ascorbic acid, however, these were found unsuitable. For example, the addition of ascorbic acid caused splitting of the non-splitted signals and the growth of one part of the splitted ones.

The cadmium concentration was evaluated by the method of standard additions and compared with the corresponding calibration curve. In most cases, the slope of the calibration curve was in good agreement with the slopes of the curves obtained by the method of standard additions (in accord with ref.[11]), but in other cases the slopes were different. This makes the method of standard additions more suitable.

For the determination of cadmium in urine, it is most recommended to use $0·03 \text{ mol } l^{-1} \text{ HNO}_3$ as modifier on electrographite. Under these conditions, the peak area of cadmium is not affected by varying concentration of NaCl. The same is true for Ta and Nb carbides layers on electrographite, except that some samples behaved anomalously. The results of urine analyses of five non-exposed persons were in the range $0·28 − 0·45 \text{ µg } l^{-1}$ Cd, for ten watched contamined persons the results were $0·82 − 1·78 \text{ µg } l^{-1}$ Cd.

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