ATOMIC ABSORPTION SPECTROMETRY OF COBALT IN THE PRESENCE OF CHELATING AGENTS

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The effect of chelating agents on the determination of cobalt in various flames, in a graphite cuvette and tantalum boat was studied considering the expected reaction mechanism of the atomization of cobalt and the reagent donor atom. A marked increase in the sensitivity of the determination of cobalt was observed in the presence of 1-(2-pyridylazo)-2-naphthol, pyrrolidinedithiocarboxylate, diethyldithiocarbamate, 8-mercaptoquinoline, 8-hydroxyquinoline and thenoyltrifluoroacetone for atomization from a tantalum boat. The optimum conditions for the determination of cobalt in the presence of 1-(2-pyridylazo)-1-naphthol are given.

The AAS of cobalt using flame and flameless techniques has been recently studied in greater detail. With nebulization of an aqueous solution of Co^{2+} in an acetylene–air flame the maximum absorbance signal was observed at 2750 K in a fuel defficient flame[1]. In reducing flames with a ratio of $C : O > 1\cdot2$ and with nebulization of cobalt complexes with a Co—C bond, the signal is decreased[2,3]; this is apparently associated with the formation of the poorly dissociating cobalt carbides during the atomization[2]. The effect of complexing agents on cobalt atomization has been observed for the Co(III) complex with O, N and C donor atoms. The maximum absorbance signal was obtained for cobalt compounds with coordinated O and C at higher observation positions than for hydrated Co^{2+} and complexing ligands with N-donor atoms[4]. A decreased signal was observed in fuel defficient flames for coordination of N in an amino- or iminogroup[5].

In a graphite cuvette the metal atoms are produced by reduction of the cobalt oxide by carbon[6,7]. Cobalt oxide is formed before appearance of the atomization signal at 1430 K (ref.[7]). No difference was found between chelates or solvates of the metals and hydrated metal ions for Cu, Ag, Zn, Cd and Pb for a large number of organic reagents with O, N and S donor atoms and for chlorinated and unchlorinated organic solvents[8]. In contrast, differences were observed between complexes in the sensitivity of determination of Cu and Ni in a graphite cuvette because of the different type of metal–donor atom (O, N, S) bond (ref.[9]).

This work describes a study of the effect of various types of chelating organic agents on the atomization of cobalt in a flame, a tantalum boat and a graphite cuvette.

EXPERIMENTAL

Solutions and Instruments

The standard solution of $0\cdot01$M cobalt acetate in methanol was prepared from anhydrous cobalt acetate (Spolek pro chemickou a hutní výrobu, Czechoslovakia) *p.a.*

The reagents employed, acetylacetone, the NH_4 salt of N-nitrosophenylhydroxylamine, (cupferron), 8-hydroxyquinoline, 8-mercaptoquinoline, 1-(2-pyridylazo)-2-naphthol (2-PAN), diphenylthiocarbazone (dithizone), sodium diethyldithiocarbamate (DDTC), thenoyltrifluoracetone (TTFA), ammonium pyrrolidinedithiocarboxylate (APDC), were of *p.a.* purity (Lachema, BDH). Methanol solutions of the chelates were prepared by mixing a standard solution of cobalt acetate in methanol with $0.01M$ reagent solution in methanol. The final concentration of the reagents for flame atomization was $5 . 10^{-4}M$ and for electrothermal atomization, $2.5 . 10^{-5}M$. The cobalt absorbance was independent of the reagent concentration up to $5 . 10^{-3}M$.

The measurements were carried out on a Perkin–Elmer 306 atomic absorption spectrophotometer with an Intensitron hollow cathode lamp heated at 30 mA. The 240·7 nm resonance line was produced by a 0·2 nm slit. During measurement of the isoabsorbance profiles of the flame, the width of the beam was adjusted by a diaphragm to a diameter of 3 mm in the middle of the burner. A 10 cm single-slit burner was used for acetylene-air or hydrogen-air flames; a triple-slit burner was used for propane-air flames.

The microsampling device, Sampling Boat System (Perkin–Elmer), with a sample size of 0·5 ml, was used for work with the tantalum boat. After placing in the boat, the methanol solutions were dried close to the flame and then atomized after inserting the boat into the flame.

Electrothermal atomization was carried out in an HGA—74 graphite cuvette. An amount of 20 µl of sample were transferred to the graphite cuvette using an Eppendorf pipette and dried at 350 K for 20 s; the decomposition time was 20 s, atomization time was 5 s, at 2870 K and an argon flow rate of 50 ml min^{-1}. The absorbance signal measured using a tantalum boat and the HGA—74 cuvette was recorded on a Zeiss G1 B1 recorder. The peak heights were measured.
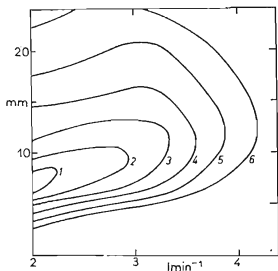

Fig. 1

The Isoabsorbance Flame Profiles for Cobalt Acetate

$5 . 10^{-5}M$ Co, air flow-rate 22·4 l min^{-1}, acetylene flow rate in litre per minute, observation height in mm. Absorbance levels from the centre: *1* 0·200; *2* 0·187; *3* 0·175; *4* 0·162; *5* 0·150; *6* 0·137.

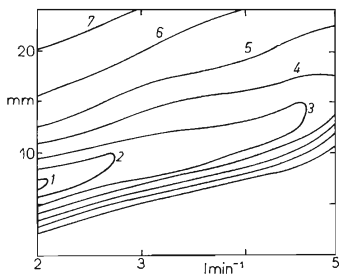Fig. 2

Isoabsorbance Flame Profiles for the Cobalt Chelate with 8-Hydroxyquinoline

$5 . 10^{-5}M$ Co, $c_L = 5 . 10^{-4}M$, air flow-rate 22·5 l min^{-1}, acetylene flow rate in l min^{-1}, observation height in mm. Absorbance levels from the centre: *1* 0·225; *2* 0·212; *3* 0·200; *4* 0·187; *5* 0·175; *6* 0·162; *7* 0·150.

RESULTS

Determination of Cobalt in an Acetylene–Air Flame

The isoabsorbance profiles for the dependences of the absorbance on the flame stoichiometry and observation height did not reveal any differences among the chelates of the organic reagents. The only difference is in the width of the absorbance zones of the chelates compared with a cobalt acetate solution (Figs 1, 2). Increased absorbance, primarily in a reducing flame, is apparent from the flame profiles of cobalt in the presence of chelating agents. The optimum parameter magnitude, air and acetylene flow-rates, and observation height in the flame are the same. Except for Co(II) acetylacetonate, the increase in the absorbance of the chelates compared with that of cobalt(II) acetate is about 8% (Table I). Together with the identical optimum flame stoichiometry, this indicates almost the same mechanism in the flame.

TABLE I

The Absorbance and Its Increase for Nebulization of the Chelate in Various Flames

$c_M = 5 . 10^{-5}$M, $c_L = 5 . 10^{-4}$M, $\Delta A = A - A_0$, A_0 is the absorbance of cobalt acetate

Co Compound	Type of bond	Acetylene–air[a]		Propane–air[b]		Hydrogen–air[c]	
		A	$100 \Delta A/A_0$	A	$100 \Delta A/A_0$	A	$100 \Delta A/A_0$
Acetate		0·209	—	0·315	—	0·255	—
Acetylacetonate	Co—O	0·214	2·4	0·312	—0·9	0·257	0·8
TTFA	Co—O	0·225	7·7	0·325	3·2	0·262	2·7
Cupferronate	Co—O	0·226	8·1	0·320	1·6	0·263	3·1
8-Hydroxyquinolate	Co—O Co—N	0·225	7·7	0·330	4·8	0·266	4·3
8-Mercaptoquinolate	Co—S Co—N	0·225	7·7	0·332	5·4	0·271	6·3
DDTC	Co—S	0·227	8·6	0·334	6·0	0·270	5·9
APDC	Co—S	0·227	8·6	0·335	6·3	0·271	6·3
Dithizonate	Co—S Co—N	0·225	7·7	0·324	2·9	0·264	3·5
2-PAN	Co—O Co—N	0·226	8·1	0·335	6·3	0·273	7·1

[a] 22·5 l min^{-1} air, 2·0 l min^{-1} acetylene, observation height in the flame, 7·5 mm, relative standard deviation of the measurement, 0·5–0·9%; [b] 0·5 l min^{-1} propane. 11·3 l min^{-1} air, observation height 7·5 mm; [c] 14·7 l min^{-1} hydrogen, 13·8 l min^{-1} air, observation height 10 mm.

Determination of Cobalt in Propane–Air and Hydrogen–Air Flames

In propane–air and hydrogen–air flames the organic reagents have only a small effect on the cobalt atomization. The absorbance increases by $5-7\%$ in the presence of 2-PAN, 8-mercaptoquinoline, APDC and DDTC (Table I).

Determination of Cobalt in a Tantalum Boat in an Acetylene–Air Flame

The absorbance signal of cobalt is substantially increased ($>10\times$) in the presence of 2-PAN, 8-mercaptoquinoline, DDTC, APDC, 8-hydroxyquinoline and TTFA. In contrast, a decrease in the absorbance signal was observed in the presence of di-thizone (Table II).

Determination of Cobalt by Atomization in a Graphite Cuvette

The curves for the thermal decomposition of the chelates practically do not differ from the curves for cobalt(II) acetate at the maximum decomposition temperature, 1100 K (Fig. 3). The curves for the decomposition of the APDC, cupferron, DDTC

TABLE II
Absorbance and Relative Increase of the Cobalt Signal in the Presence of Organic Reagents for Measurements Using a Tantalum Boat[a]
$c_M = 4 \cdot 10^{-5}$M Co, $c_L = 5 \cdot 10^{-4}$M.

Co Compound	Bond type	A	A/A_0[b]
Acetate		0·035	1·0
Acetylacetonate	Co—O	0·173	5·0
TTFA	Co—O	0·388	11·1
Cupferronate	Co—O	0·148	4·3
8-Hydroxyquinolate	Co—O Co—N	0·443	12·7
8-Mercaptoquinolate	Co—S Co—N	0·555	15·9
DDTC	Co—S	0·528	15·1
APDC	Co—S	0·475	13·8
Dithizonate	Co—S Co—N	0·020	0·6
2-PAN	Co—O Co—N	0·555	15·9

[a] Boat height in the flame, 5 mm, observation height above the boat bottom, 10 mm (optimal height), 26·0 l min^{-1} air, 4·8 l min^{-1} acetylene; [b] A_0 absorbance of cobalt acetate.

TABLE III

Absorbance and Relative Increase in the Signal in the Electrothermal Atomization at 2·870 K
$c_M = 4 . 10^{-6}$M, $c_L = 2·5 . 10^{-5}$M, decomposition 20 s at 1 100 K, $\Delta A = A_{chelate} - A_0$, A_0
absorbance of cobalt acetate.

Co Compound	Bond type	A	$100 \Delta A/A_0$
Acetate		0·191	
Acetylacetonate	Co—O	0·194	1·6
TTFA	Co—O	0·195	2·1
Cupferronate	Co—O	0·228	19·4
8-Hydroxyquinolinate	Co—O, Co—N	0·233	22·0
8-Mercaptoquinolinate	Co—S, Co—N	0·230	20·4
DDTC	Co—S	0·227	18·8
APDC	Co—S	0·232	21·5
Dithizonate	Co—S, Co—N	0·228	19·4
2-PAN	Co—O, Co—N	0·234	22·5

TABLE IV

Sensitivity of the Determination, Characteristic Concentration and Detection Limit for Atomization of Cobalt in the Presence of 2-PAN[a]

Value	Acetylene–air flame	Graphite cuvette	Tantalum boat
Characteristic concentration[b]	$8 . 10^{-7}$M	$6·8 . 10^{-8}$M	$2·8 . 10^{-7}$M
Detection limit[c]	$5·2 . 10^{-7}$M	$8·8 . 10^{-8}$M	$1·7 . 10^{-7}$M
Sensitivity of the determination[d]	$5\ 000$M^{-1}	$58\ 500$M^{-1}	$14\ 200$M^{-1}
Linearity of the calibration curve	$5·2 . 10^{-7}$—$5 . 10^{-5}$M $30·7$—$2\ 950$ µg l^{-1}	$8·8 . 10^{-8}$—$5 . 10^{-6}$M $5·2$—295 µg l^{-1}	$1·7 . 10^{-7}$—$1·5 . 10^{-5}$M 10—885 µg l^{-1}
Relative standard deviation in the linear region of the calibration curve	$2·6$—$0·5\%$	$6·5$—$2·6\%$	$6·8$—$1·1\%$

[a] $c_L = 4 . 10^{-5}$M; [b] characteristic concentration for the value of $A = 0·004$; [c] the detection limit is the concentration corresponding to $A = \overline{A}_{blank} + 3s_{blank}$, where s_{blank} is the standard deviation of the blank for 10 measurements; [d] the determination sensitivity corresponds to the slope of the calibration dependence for $c_M \to 0$.

and dithizone chelates are analogous to the curves for the 2-PAN and 8-hydroxy-quinoline chelates. Comparison of the chelate absorbance with that of cobalt(II) acetate is given in Table III. The relative standard deviation for five measurements of $4 . 10^{-6}M$ Co was $2.4 - 4.5\%$. In the presence of cupferron, 8-hydroxyquinoline, 8-mercaptoquinoline, DDTC, APDC, dithizone and 2-PAN the absorbance signal for cobalt increases by about 20%.

DISCUSSION

The relative increase in the absorbance signal of cobalt during atomization in a tantalum boat in the order 8-mercaptoquinoline = 2-PAN > DDTC > APDC > > 8-hydroxyquinoline > TTFA > acetylacetonate > cupferronate > dithizonate is in partial agreement with the volatility of these chelates. The chelates of cobalt with DDTC, APDC, TTFA volatilize at approx. 500 K, the acetylacetonate at 700 K and the 8-hydroxyquinoline, cupferron and dithizone chelates volatilize only with difficulty[10].

With electrothermal atomization in a graphite cuvette, vaporization at a temperature of 1 100 K would result in a decrease in the absorbance signal of cobalt. As this does not occur and the signal is even larger than that for cobalt(II) acetate, apparently CoO or another compound, e.g. CoS, is formed on the graphite surface[11]. Apparently the effect of the carbon from the organic reagent on the reduction of CoO is reflected in the increase in the signal by 20% in the presence of most organic reagents during atomization of Co in a graphite cuvette. In atomization of cobalt from a graphi-
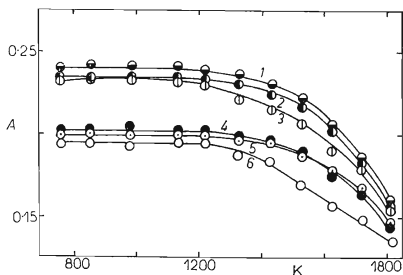

Fɪɢ. 3

Curves for the Thermal Decomposition of Cobalt Chelate in a Graphite Cuvette (atomization 5 s at 2·870 K, decomposition 20 s, $4 . 10^{-6}M$ Co, $c_L = 2.5 . 10^{-5}M$)

1 2-PAN, *2* 8-hydroxyquinolinate, *3* 8-mercaptoquinolinate, *4* acetylacetone, *5* TTFA, *6* acetate.

te cuvette with a tantalum foil, which removes the effect of the graphite, a broad, low peak was obtained, as a slowly vaporizing compound with tantalum is formed[12]. This effect was not observed using a flame and a tantalum boat, as the temperature increases more rapidly during atomization from a tantalum boat placed in a flame.

During nebulization in the flame, CoO is most probably formed. Cobalt oxide dissociates in the flame. The reduction by the H, CO, C, CH and C_2 species in the acetylene–air and propane–air flames and by the H species in the hydrogen–air flame apparently plays a role in the atomization. In an acetylene–air flame with a temperature of 2550 K the organic reagent has only a small effect on the cobalt atomization, increasing it by about 8%. With the cooler propane–air flame at 2200 K and with the hydrogen–air flame containing only H-species, the organic reagents had an even smaller effect on the cobalt atomization, with a maximal atomization increase of $6-7\%$.

Determination of Cobalt in the Presence of 2-PAN

During atomization of cobalt in a flame, a graphite cuvette and primarily a tantalum boat, the greatest determination sensitivity was attained in the presence of 2-PAN. The sensitivity of the determination, characteristic concentration and the detection limit for the individual types of atomization are given in Table IV.

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