THE ATOMIC ABSORPTION SPECTROMETRY OF MOLYBDENUM IN THE PRESENCE OF SULPHONATED AROMATIC COMPOUNDS

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The effect of sulphonated aromatic compounds on the atomization of molybdenum in acetylene–air and nitrous oxide–acetylene flames was studied. The absorbance signal is increased in the presence of these compounds only in acetylene–nitrous oxide flames and in the presence of potassium or sodium salts. Otherwise, the absorbance is decreased. The probable mechanism of the effect of sulphonated aromatic groups during the atomization of molybdenum is discussed. The determination in the presence of 0.1 M 5-sulphosalicylic acid and 9.5 mg ml^{-1} KCl is without interference and has high sensitivity.

The sensitivity of the determination of molybdenum by AAS is greater when organomolybdenum compounds are used than with inorganic compounds with an oxygen bond[1]. After vaporization in the flame, molybdenum compounds can dissociate or be reduced to free molybdenum atoms. However, the reduction of molybdenum compounds in the condensed phase can lead to the formation of molybdenum and its carbide in the same phase and thus to a decrease in the concentration of gaseous molybdenum atoms in the flame[2,3]. The degree of vaporization and reduction thus determine the sensitivity of the determination. As the volatility of molybdenum and its carbide is lower than that of molybdenum oxide, the determination of molybdenum is disturbed strongly by a number of elements where the formation of thermally stable compounds of molybdenum with the accompanying metal can also occur[4].

This work deals with the effect of selected organic reagents, especially sulphonated aromatic compounds, on the determination of molybdenum and in suppressing interferences during determination in a flame.

EXPERIMENTAL

Chemicals and Instruments

The standard molybdenum solution containing 0.966 g l^{-1}, *i.e.* $1 . 10^{-2}$ M-Mo, was prepared by dissolving $(NH_4)_6Mo_7O_{24}.4 H_2O$ *p.a.* in distilled water and was standardized gravimetrically on the basis of $MoO_2(C_9H_6ON)_2$.

Molybdenum was determined using a Perkin-Elmer 306 AAS spectrophotometer at a wavelength of 313.3 nm with a slit width of 0.7 nm. The Intensitron hollow cathode lamp heated by 30 mA produced a beam with a diameter of 6 mm in the centre of the flame (the large area

technique). The isoabsorbance profile of the flame was investigated using an aperture with a diameter of 3 mm in the centre of the flame (the small area technique).

The organic reagents. phenol, pyrocatechol, pyrogallol, the potassium salt of pyrogallolsulphonic acid, 5-sulphosalicylic acid, the disodium salt of chromotropic acid, the potassium salt of pyrogalloldisulphonic acid, the disodium salt of pyrocatechol-3,5-disulphonic acid and the disodium salt of naphthalene-1,5-disulphonic acid were of *p.a.* purity or were recrystallized from aqueous solutions.

Conditions for the Determination

The optimum conditions for the determination of molybdenum in the presence of sulphonated aromatic compounds in an acetylene–air flame differ very little from those for a molybdenum solution. They were, however, very different in an acetylene–nitrous oxide flame. In Figs 1 and 2 are depicted the isoabsorbance profiles, *i.e.* the dependences giving the same absorbance level for the observation height and flame stoichiometry for the atomization of molybdenum in the presence of sulphonated and unsulphonated aromatic compounds, pyrocatechol-3,5-disulphonic acid
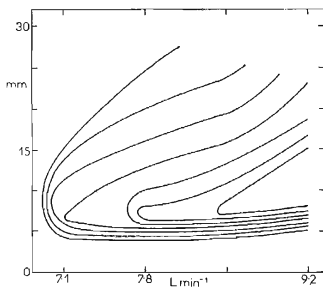

FIG. 1

The Isoabsorbance Profile of Molybdenum in the Presence of Pyrocatechol.

$4 \cdot 10^{-4}$M Molybdenum and $8 \cdot 10^{-3}$M pyrocatechol, nitrous oxide flow-rate 11·8 l. . min^{-1}; the absorbance levels are from $A = 0\cdot200$ to $0\cdot350$ in steps of $0\cdot025$, the observation height is given in mm, the acetylene flow-rate in l min^{-1}.
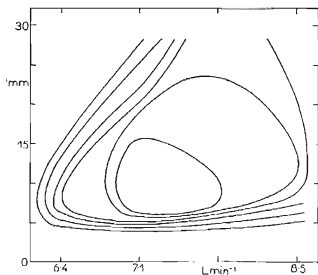
FIG. 2

The Isoabsorbance Profile of Molybdenum in the Presence of Pyrocatechol-3,5-disulphonic Acid in an Acetylene–Nitrous Oxide Flame

$4 \cdot 10^{-4}$M-Mo, $0\cdot05$M disodium pyrocatechol-3,5-disulphonate, nitrous oxide flow-rate 11·8 l min^{-1}; absorbance levels are $A = 0\cdot150$, $0\cdot200$, $0\cdot250$, $0\cdot275$, $0\cdot300$ and $0\cdot325$. The observation height is given in mm, acetylene flow-rate in l min^{-1}.

and pyrocatechol. The isoabsorbance profile of a molybdate solution was similar to the profile of molybdenum in the presence of pyrocatechol in Fig. 2. The concentration of molybdenum atoms in the flame is very dependent on its stoichiometry and on the observation height, which is also reflected in the different conditions for 6 mm and 3 mm beams from the hollow cathode lamp. For the acetylene–air flame (air flow-rate $22 \cdot 6 \, l \, min^{-1}$) and using the large-area technique, the optimal acetylene flow-rate was $6 \cdot 1 \, l \, min^{-1}$ and the optimum observation height was $14 \cdot 5$ mm above the burner for molybdate both in the presence and absence of aromatic compounds. Using the small-area technique, an acetylene flow-rate of $6 \cdot 8 \, l \, min^{-1}$ and observation height of $13 \cdot 5$ mm were used for molybdate both in the presence and absence of pyrocatechol. A height of 16 mm was used for molybdate in the presence of pyrocatechol-3,5-disulphonic acid. In an acetylene–nitrous oxide flame with a nitrous oxide flow-rate of $11 \cdot 8 \, l \, min^{-1}$ and using the large-area technique, the optimal observation height was $7 \cdot 5$ mm and an acetylene flow-rate of $9 \cdot 4 \, l \, min^{-1}$ for molybdate, $8 \cdot 6 \, l \, min^{-1}$ for molybdate in the presence of pyrocatechol and $6 \cdot 4$ $l \, min^{-1}$ in the presence of pyrocatechol-3,5-disulphonic acid. Using the small-area technique in an acetylene–nitrous oxide flame, the optimum observation height was $9 \cdot 5$ mm and the acetylene flow-rate was $10 \cdot 1 \, l \, min^{-1}$ for molybdate and $9 \cdot 4 \, l \, min^{-1}$ for molybdate in the presence of pyrocatechol; however, the optimum values in the presence of pyrocatechol-3,5-disulphonic acid were an observation height of $7 \cdot 0$ mm and an acetylene flow-rate of $7 \cdot 1 \, l \, min^{-1}$. In the presence of sulphonated aromatic compounds molybdenum is atomized in a fuel-poor acetylene–nitrous oxide flame better than for atomization of molybdate.

The Effect of the Reagent Concentration on the Molybdenum Atomization

At low concentrations of sulphonated aromatic compounds (at reagent : molybdenum ratios of $1 : 1 - 2 : 1$), the molybdenum absorbance decreases rapidly in both acetylene––air and acetylene–nitrous oxide flames (Fig. 3). With increasing sulphonated aromatic compound concentrations, the absorbance in acetylene–air flames does not change, while that in acetylene–nitrous oxide flames increases very slightly. Unsulphonated aromatic compounds have different effects. Phenol and pyrocatechol affect the absorbance only slightly in acetylene–air flames, whereas they increase the absorbance in acetylene–nitrous oxide flames. Pyrogallol behaves analogously to sulphonated reagents in both flames.

At larger excesses of aromatic sulphocompounds in an acetylene–air flame at reagent : molybdenum ratios > 15 and in acetylene–nitrous oxide flames at ratios > 3, the absorbance increases in the presence of potassium or sodium salts (Fig. 4 and 5). The absorbance increase in acetylene–air flames is less than in acetylene–nitrous oxide flames, where the sensitivity of the determination of molybdenum is doubled

in the presence of 0·1M sulphonated aromatic compounds. Among phenols, the absorbance in the presence of pyrogallol is increased in the presence of potassium or sodium salts, but is still lower than that for sulphonated aromatic compounds. The sensitivity of the determination increased in the presence of all the tested sulphonated reagents (at 0·1M concentration and with addition of 1 mg ml^{-1} Na$^+$ or K$^+$), *i.e.* sulphosalicylic acid, chromotropic acid, pyrocatechol-3,5-disulphonic acid, naphthalene-1,5-disulphonic acid, pyrogallol sulphonic acid and pyrogallol disulphonic acid.

The concentration of the Na$^+$ or K$^+$ salt also determines the degree of increase in the sensitivity of the determination. The maximum increase in the sensitivity of the determination of molybdenum in the presence of sulphosalicylic acid was attained
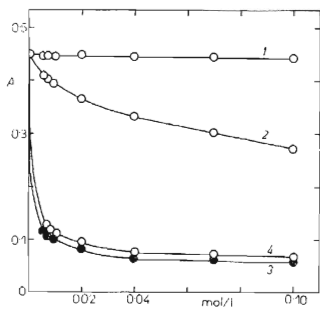

FIG. 3

The Dependence of the Molybdenum Absorbance on the Concentration of Aromatic Compounds in the Acetylene–Air Flame

4 . 10^{-4}M-Mo, air flow-rate 22·6 l min^{-1}, acetylene 6·1 l min^{-1}, observation height 14·5 mm; *1* phenol, *2* pyrocatechol, *3* pyrogallol, *4* sulphosalicylic acid.
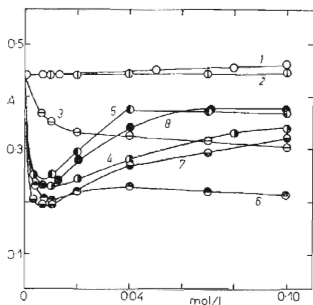
FIG. 4

The Dependence of the Molybdenum Absorbance on the Concentration of Aromatic Compound in the Presence of KCl in the Acetylene–Air Flame

4 . 10^{-4}M-Mo, 2 mg ml^{-1} KCl, acetylene flow-rate 6·1 l min^{-1}, air 22·6 l min^{-1}, observation height 14·5 mm; *1* phenol, *2* pyrocatechol, *3* pyrogallol, *4* pyrogallolsulphonic acid, potassium salt, *5* potassium salt of pyrogalloldisulphonic acid, *6* sulphosalicylic acid, *7* disodium salt of chromotropic acid, *8* disodium salt of pyrocatechol-3,5-disulphonic acid.

at a ratio of reagent : K^+ = 0·78. KCl alone at a concentration of 2 mg ml^{-1} decreases the absorbance of molybdenum in an acetylene-nitrous oxide flame by 26%.

Calibration Dependences

The sensitivity of the determination is increased in the presence of sulphonated aromatic compounds only in acetylene–nitrous oxide flames. The calibration curves are linear up to $1·5 . 10^{-5}$ M-Mo. The characteristic concentrations and detection limits are given in Table 1. It follows from this table that the characteristic concentrations for the reagents used are roughly the same; the detection limit is best for the determination of Mo in the presence of sulphosalicylic acid. The determination of Mo in the presence of sulphonated aromatic compounds is twice as sensitive as in the absence of these reagents. It should, however, be noted that determinations in the presence of sulphonated aromatic compounds should be carried out in a flame with less fuel than the optimal flame for molybdate alone, in which the determination sensitivity is lower. Measurement is easier in fuel-lean flames.

Interferences

The interfering effect of Al^{3+}, Fe^{3+}, Cr^{3+}, Ca^{2+}, Sr^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} in the determination of molybdenum can be suppressed using chromotropic acid, naphthalene-1,5-disulphonic acid, pyrocatechol-3,5-disulphonic acid and sulphosalicylic acid in 0·05M concentrations. At a higher concentration of interfering element, 1 mg ml^{-1}, and for $1·4 . 10^{-4}$ M-Mo, the intereference of the cations could not be completely eliminated using any of these reagents. Sulphosalicylic acid was most effective. Sulphosalicylic acid at a concentration of 0·1M and in the presence of 9·5 mg .
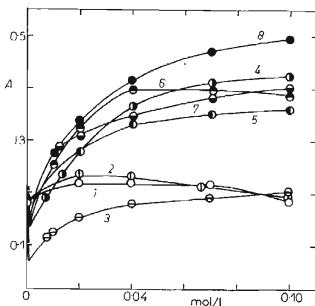

FIG. 5

The Dependence of the Molybdenum Absorbance on the Concentration of Aromatic Compound in the Presence of KCl in an Acetylene–Nitrous Oxide Flame

$4 . 10^{-4}$ M-Mo, 2 mg ml^{-1} KCl, acetylene flow-rate 6·4 l min^{-1}, nitrous oxide 11·8 l min^{-1}, observation height 7·5 mm.

1 Phenol, *2* pyrocatechol, *3* pyrogallol, *4* pyrogallolsulphonic acid, potassium salt, *5* potassium salt of pyrogalloldisulphonic acid, *6* sulphosalicylic acid, *7* disodium salt of chromotropic acid, *8* pyrocatechol--3,5-disulphonic acid, disodium salt.

. ml^{-1} KCl completely eliminated the interference of Al^{3+}, Fe^{3+}, Cr^{3+}, Ca^{2+}, Sr^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} in the determination of $\leq 3 . 10^{-5}$M-Mo, even at a cation concentration of 1 mg ml^{-1}. In the determination of $\leq 1.4 . 10^{-4}$M-Mo, Al^{3+}, Ca^{2+} and Sr^{2+} do not interfere up to a concentration of 0.2 mg ml^{-1} and Fe^{3+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} up to 1 mg ml^{-1}.

An important role in the suppression of interferences is played by the ratio of the reagent concentration to the concentration of interfering element, as can be illustrated on the example of supression of the effect of Ca^{2+} and Sr^{2+} by sulphosalicylic acid. The interference of 0.2 mg ml^{-1} Ca^{2+} and Sr^{2+} in the determination of 1.4 . 10^{-4}M-Mo was eliminated by addition of 0.09M sulphosalicylic acid. The interference of 1 mg ml^{-1} Ca^{2+} and Sr^{2+} in the determination of 1.4 . 10^{-4}M-Mo could not be eliminated even by 0.15M sulphosalicylic acid.

The Atomization Mechanism

The mechanism of the atomization of molybdenum in the presence of sulphonated aromatic compounds was studied on the model of sulphosalicylic acid.

The presence of sulphosalicylic acid up to a concentration of 0.1M in the presence and absence of KCl up to a concentration of 9.5 mg ml^{-1} did not affect the nebulization efficiency. Similarly, it did not affect the lateral diffusion of molybdenum, as was confirmed by measurement of the horizontal flame profile and measurements with the flame turned perpendicular to the optical axis.

TABLE I

The Characteristic Concentrations and Detection Limits for the Determination of Molybdenum in the Presence of Sulphonated Aromatic Compounds in an Acetylene–Nitrous Oxide Flame[a]

Acid	Characteristic concentration[f]		Detection limit[g]	
	$M . 10^6$	$\mu g \, ml^{-1}$	$M . 10^6$	$\mu g \, ml^{-1}$
—	7.0	0.67	4.0	0.38
Pyrocatechol-3,5-disulphonic[b,c]	3.0	0.29	2.9	0.28
Pyrogallolsulphonic[d,c]	3.1	0.30	4.0	0.38
Chromotropic[b,2]	3.3	0.31	3.1	0.30
Sulphosalicylic[e]	3.1	0.30	1.4	0.13

[a] Acetylene flow-rate 6.4 l min^{-1}, nitrous oxide 11.8 l min^{-1}, observation height 7.5 mm; [b] disodium salt; [c] plus 2 mg ml^{-1} KCl; [d] potassium salt; [e] plus 9.5 mg KCl ml^{-1}; [f] the characteristic concentration yields $A = 0.004$; [g] the detection limit is the concentration corresponding to $A = \overline{A} + 3s_{blank}$, where s_{blank} is the standard deviation of the blank found from 18 measurements.

Using two nebulizers, the effect of sulphosalicylic acid and KCl with combined and individual nebulization of the solution into the flame were compared (Tables II and III). The absorbance of molybdenum is decreased in the presence of sulphosalicylic acid at a concentration corresponding to $3 \cdot c_{Mo}$ in both flames primarily through reaction in the condensed phase. At concentrations corresponding to $125 \cdot c_{Mo}$, reactions occurring in the gaseous phase become important in both flames, as well as the reaction in the condensed phase for the acetylene–air flame. The relative increase in the molybdenum signal in the acetylene–air flame in the presence of sulphosalicylic acid and KCl is a result of reaction in the gaseous phase. The increase in the sensitivity of the determination of molybdenum in the acetylene–nitrous oxide flame in the presence of sulphosalicylic acid at a concentration corresponding to $125 \cdot c_{Mo}$ and KCl is a result of the reaction in both the gaseous and condensed phases.

The dependence of the absorbance of molybdenum on the concentration of sulphosalicylic acid has the character of chemical interference (Fig. 3). Continuous variation of solutions of molybdenum and sulphosalicylic acid ($c_0 = 4 \cdot 10^{-4}$M) exhibited a maximum of the plot $\Delta A_{flame} = f c_L / c_{0 \text{ solution}}$ at a ratio of sulphosalicylic acid : : Mo = 1 : 1·66 for both acetylene–air and acetylene–nitrous oxide flames (ΔA is the

TABLE II

The Effect of Sulphosalicylic Acid and Potassium on the Atomization of Molybdenum Using Two Nebulizers[a]

Reagent	Flame			
	acetylene–air[b]		acetylene–nitrous oxide[c]	
	A%[d]	B%	A%	B%
Sulfosalicylic acid, $1\cdot2 \cdot 10^{-3}$M	47	81	58	82
Sulphosalicylic acid, 0·05M	39	55	80	79
KCl, 1 mg ml^{-1} K$^+$	99	104	72	100

[a] Nebulization according to the scheme

	Nebulizer	
	I	II
A	Mo + reagent	water
B	Mo	reagent

[b] Acetylene flow-rate, 5·1 l min^{-1}, air 18·8 l min^{-1}, observation height 14·5 mm; [c] acetylene flow-rate 6·4 l min^{-1}, nitrous oxide 11·8 l min^{-1}, observation height 7·5 mm; [d] % are related to the absorbance of Mo in water, $A_{Mo} = 100\%$, $c_{Mo} = 4 \cdot 10^{-4}$M.

decrease in the absorbance compared to Mo in the absence of sulphosalicylic acid). At this ratio of sulphosalicylic acid and molybdenum in the flame, atomization of molybdenum in the flame is suppressed most.

DISCUSSION

In solutions containing polyphenols, molybdate forms a number of coloured complexes in dependence on the pH and reagent concentration[5]. However, because sulphonated aromatic compounds without OH groups and naphthalene-1,5-disulphonic acid have the same effect on the determination of molybdenum as sulphonated phenols with OH groups in the *ortho* and *peri* positions, the decisive reaction apparently occurs during the formation or vaporization of the aerosol rather than in the solution. Thus the properties and stabilities of the complexes in solution are not decisive in the effect of these organic reagents on the sensitivity of the AAS determination.

Thus the decrease in the atomization of the molybdenum compounds in the flame can be attributed to the formation of molybdenum carbide, Mo_2C, or molybdenum

TABLE III

The Effect of Sulphosalicylic Acid in the Presence of Potassium on the Atomization of Molybdenum Using Two Nebulizers[a]

Concentration of sulphosalicylic acid, M	Flame							
	acetylene–air[b]				acetylene–nitrous oxide[c]			
	A %[d]	B %	C %	D %	A %	B %	C %	D %
$1·2 . 10^{-3}$	61	58	92	95	50	69	69	92
0·05	52	52	66	74	152	95	75	100

[a] Nebulization according to the scheme:

	Nebulizer	
	I	II
A	Mo + reagent + K[+e]	water
B	Mo + reagent	K^{+}
C	Mo + K^{+}	reagent
D	Mo	reagent + K^{+}

[b] Acetylene flow-rate $5·1 \, l \, min^{-1}$, air $18·8 \, l \, min^{-1}$, observation height $14·5$ mm; [c] acetylene flow-rate $6·4 \, l \, min^{-1}$, $N_2O \, 11·8 \, l \, min^{-1}$; observation height $7·5$ mm; [d] % are related to the absorbance of Mo in water, $A_{Mo} = 100\%$, $c_{Mo} = 4 . 10^{-4} M$; [e] KCl, 1 mg ml^{-1} K$^+$.

in the condensed phase[2,3]. This reaction can also occur as a result of the effect of the carbon in the aromatic compound. In addition to vaporization of molybdenum oxide, further reactions can occur:

$$2\,MoO_{(s,l)} + 3\,C_{(s)} \rightarrow Mo_2C_{(s,l)} + 2\,CO \qquad (A)$$

$$MoO_{(s,l)} + C_{(s)} - Mo_{(s,l)} + CO \qquad (B)$$
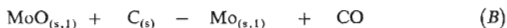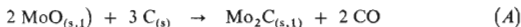
In the presence of potassium or sodium and sulphosalicylic acid (and thus other naphthol or phenol sulphonated acids), probably K_2SO_4 or Na_2SO_4 is formed in the flame and oxidizes $Mo_{(s,l)}$ or $Mo_2C_{(s,l)}$ to $MoO_{(s,l)}$:

$$3\,Mo_{(s,l)} + 2\,K_2SO_4 \rightarrow 2\,K_2MoO_4 + MoS_2 \qquad (C)$$

$$3\,Mo_{(s,l)} + 2\,Na_2SO_4 \rightarrow 2\,Na_2MoO_4 + MoS_2 \qquad (D)$$
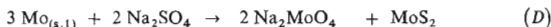
Thus, after vaporization of MoO, free gaseous atoms of molybdenum are formed from molybdate. Consequently, the gaseous products of decomposition of sulphonated aromatic compounds can affect the atomization of molybdenum. The different optimal stoichiometry of the acetylene–nitrous oxide flame also confirms that the reaction occurs in the gaseous phase.

Determination of Molybdenum by AAS in the Presence of Sulphosalicylic Acid

A solution with a molybdenum concentration of $<15\ \mu g\ ml^{-1}$, which also contains $0.1\,M$ sulphosalicylic acid and $9.5\ mg\ ml^{-1}$ KCl is nebulized into an acetylene–nitrous oxide flame with an acetylene flow-rate of $6.4\ l\ min^{-1}$ and a nitrous oxide flow-rate of $11.8\ l\ min^{-1}$ and the absorbance is measured at an observation height of 7.5 mm. The detection limit is $0.13\ \mu g\ ml^{-1}$ Mo. In the measurement it is necessary to subtract or eliminate, using the deuterium correction, the nonselective absorption produced by the mixture of sulphosalicylic acid and KCl($A = 0.006$).

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