

THE PHENOMENAL INTERFERENCE ON THE ATOMIC ABSORPTION OF MANGANESE CHROMIUM AND NICKEL

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The phenomenal effect of polymeric formations on the atomic absorption of manganese, chromium and nickel in cool flames, is a harmful effect due to the inclusion of the analyte inside the heteropoly anion lattice. The way to get rid of such interference rests with the addition of a laboratory synthesized ligand to the sample solution to deform heteropoly formation, thus shifting the equilibrium in favour of normalizing free atoms in the flame.

Key words: Polymeric formations; Manganese; Chromium and Nickel.

INTRODUCTION

Atomic absorption is unquestionably one of the most sensitive of all analytical methods. In cool flames, sensitivity is indirectly hindered by inhibitory effects as compound formation with the analyte in the flame [1-3] or in the solution [4].

Literature reveals that some of the interferences are generally found by all investigators [5] while some others are found occasionally under particular circumstances [6-8].

This observation leads to a classification of interferences thus encountered (1) The properties of the analyte which may give rise to dry particles of compounds formed between the analyte and concomitants with different thermochemical properties. The physical properties of most concern in these cases are the melting and boiling points of these compounds [9-11]. To this type of interference the term *inherent interference* can be applied. (2) Sample pretreatment and percentage concomitants

which impart some characteristics to the analyte behaviour in the flame and affect the occurrence and magnitude of the interference. This type of interference may be termed *phenomenal interference* and takes place essentially due to formation of polymeric entities, complex compounds, selective association, co-precipitation, etc. This rests primarily on the postulation that the analyte does not participate in such formations but is influenced by their presence during the process of nebulization. In other words, as the possibility of existence of specific species with the dry aerosol is introduced, the analyte may be occluded in their structures. Consequently, its rate of vaporization in the flame is depressed by the large size and other physical properties of the dry aerosol particle.

The present work substantiates the phenomenal interference by investigating the role of heteropolymeric formations as serious depressive cause on the absorption of manganese, chromium and nickel. The way to eliminate the formation of these structures is also discussed.

Table 1. The optimal instrumental conditions for the determination of manganese, chromium and nickel.

Element	Instrumental conditions					
	Wavelength (nm)	Lamp current (mA)	Slit width (mm)	Air flow rate (dm ³ /min)	Acetylene flow rate (dm ³ /min)	Burner height (cm*)
Mn	279.5	12	0.15	5	1.5	0.8
Cr	357.9	10	0.15	5	1.8	1.0
Ni	232	15	0.10	5	1.2	0.6

*The distance from the top of the burner to "grazing incidence position". Type of the flame was stoichiometric-fuel - rich, fuel - rich-luminous and stoichiometric for manganese, chromium and nickel respectively.

MATERIALS AND METHODS

AR grade acids were used throughout. Stock solutions* were prepared as chlorides or nitrates; molybdenum solution was prepared from ammonium molybdate tetrahydrate; aliquots were suitably diluted to give the desired metal concentrations used for the experiments.

(i) A Unicam SP 90A, series 2 atomic absorption spectrophotometer, which incorporated a SP 91 lamp turret accessory. Air was supplied through an SP 93 air compressor, and acetylene was obtained from cylinders after passing through conc. sulphuric acid and glass wool for purification. Table 1 shows the operational settings used throughout. (ii) A Unicam SP 1800 ultraviolet spectrophotometer, with 1 cm³ stoppered silica cells. (iii) A Perkin-Elmer 557 infrared spectrophotometer using polyethylene discs.

One cm³ of the analyte stock solution (1 cm³ = 100, 500 or 100 µg) of manganese, chromium or nickel respectively was placed in a 10 cm³ volumetric flask. The interfering ion(s) solution(s) plus nitric or hydrochloric acid were added in appropriate amounts and diluted to the mark with deionized bidistilled water. The absorbance of the mixture was compared to that of the analyte solution only.

RESULTS AND DISCUSSION

Interference of heteropoly ions. Interference study of molybdenum and rhodium on the absorption of manganese, chromium and nickel in neutral or 0.1M of nitric, sulphuric, hydrochloric or perchloric acid indicated insignificant change. Unlike these acids, σ -phosphoric acid do cause depressive effect on the absorption of the three analytes in the presence of molybdenum or rhodium as illustrated in Fig. 1-3. The effect is very conspicuous in the case of manganese.

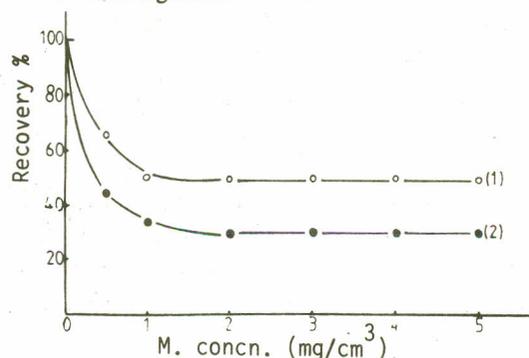


Fig. 1. Effect of Mo or Rh on the recovery of 10 µg/cm³ of Mn from 0.1M phosphoric acid solution, M = (1) MO and (2) Rh.

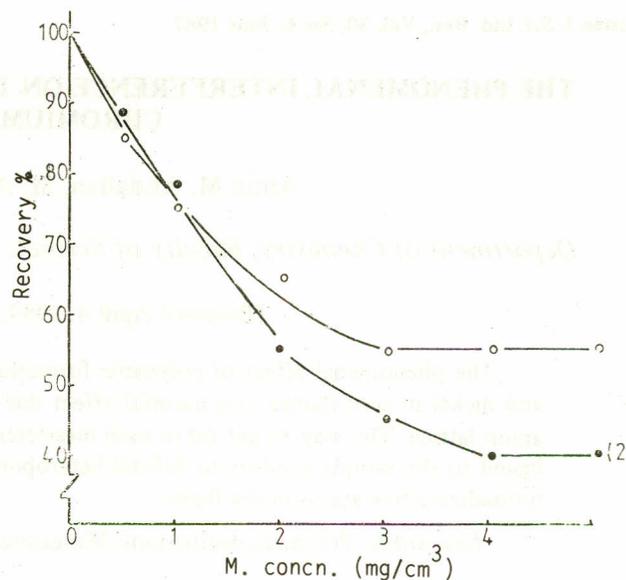


Fig. 2. Effect of Mo or Rh on the recovery of 50 µg/cm³ of Cr from 0.1 M phosphoric acid solution, M = (1) Mo and (2) Rh.

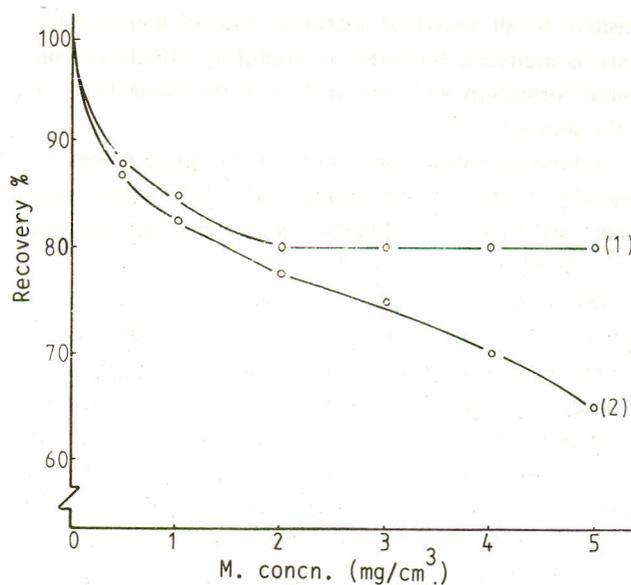


Fig. 3. Effect of Mo or Rh on the recovery of 10 µg/cm³ of Ni from 0.1 M phosphoric acid solution, M = (1) Rh and (2) Mo.

Changes in the hydrogen ion concentration of the analyte solution (pH from 1 to 4) and in the order of mixing of the reagents did not result in any improvement in analyte absorption.

For similar preparations, extraction was employed quantitatively by ether. Aspiration of the aqueous layer had indicated the restoring of the analyte signal to that of the analyte solution only. This may imply, (i) formation of a heteropoly anion species and that (ii) the analyte was not a component in the heteropoly anion lattice.

*Water was always supplied from a Fi-stream 4 dm³ hr⁻¹ deionization and bi-distillation water still - 4 BD Still No. 2707/C.

The result of the influence of digestion (on a water bath for 24 hr) is presented in Table 2. The data show consistent improvement in manganese recovery. This means that the lattices of the heteropoly anion species become more regular in character after digestion, thus resulting in a decrease in the area of their surfaces and consequent reduction in the inclusion of manganese.

Table 2. Effect of digestion on the recovery of $10 \mu\text{g}/\text{cm}^3$ of manganese from solutions of $0.1\text{M H}_3\text{PO}_4$ containing molybdenum or rhodium.

No.	Solution	Recovery (%)	
		Before digestion	After digestion
1	$10 \mu\text{g}/\text{cm}^3$ of Mn + $0.1\text{M H}_3\text{PO}_4$	100	100
2	solution 1 + $1 \text{ mg}/\text{cm}^3$ of Mo	50	72.9
3	solution 1 + $0.5 \text{ mg}/\text{cm}^3$ of Rh	45	72.9

The infrared spectra of the mixture, $10 \mu\text{g}$ of manganese, 1 mg of molybdenum plus 0.1M σ -phosphoric acid per 1 cm^3 , before and after digestion, in the region $4000 - 200 \text{ cm}^{-1}$ was carried out in polyethylene disc and recorded on charts of Fig. 4 and 5. The interpretation of the spectra [12] of the mixture in both cases indicates that the nature of the analyte manganese is largely altered, since after digestion it is heavily coordinated; hence its volume is increased opposing its inclusion in the heteropoly anions cavities.

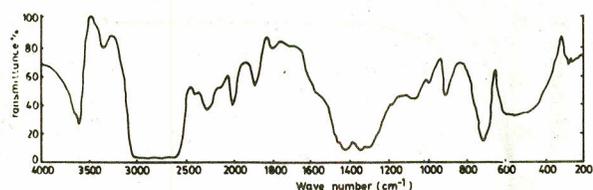


Fig. 4. Infrared spectra for phosphomolybdate* anion in the presence of $10 \mu\text{g}/\text{cm}^3$ of manganese before digestion.

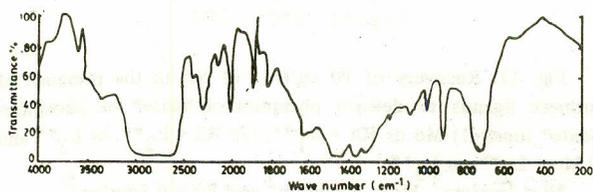


Fig. 5. Infrared spectra for phosphomolybdate* anion in the presence of $10 \mu\text{g}/\text{cm}^3$ of manganese after digestion.
*P = $3 \text{ mg}/\text{cm}^3$ and Mo = $1 \text{ mg}/\text{cm}^3$.

The phenomenal effect of other heteropoly formations was investigated. The curves of Fig. 6-10 show the harmful effect of such formations on the absorption of manganese. For the sake of clarity, the numbers of the curves in Fig. 6, 7, 9 and 10 were reduced and the plots are the means of the results (± 5 recovery units) just to

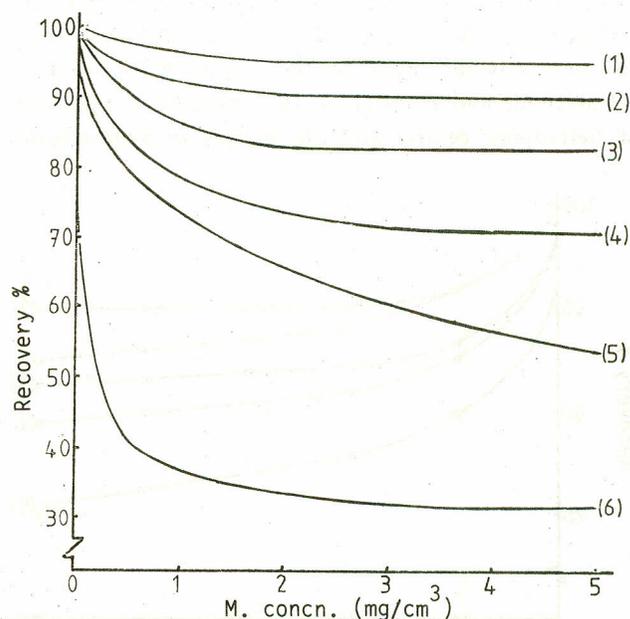


Fig. 6. Effect of $\text{Si}^*\text{-M}$ heteropoly anion formation on the recovery of $10 \mu\text{g}/\text{cm}^3$ of Mn from 0.1 M hydrochloric acid solution, M = (1) Zn, (2) Sn, Cr, Al, In, Ga or Rh, (3) Ge, Ti, V, As, Ph, Cd, Hg, W or Tl, (4) Sb, Ni, Cu or Bi, (5) Mo and (6) Sc.

*Si = $1 \text{ mg}/\text{cm}^3$.

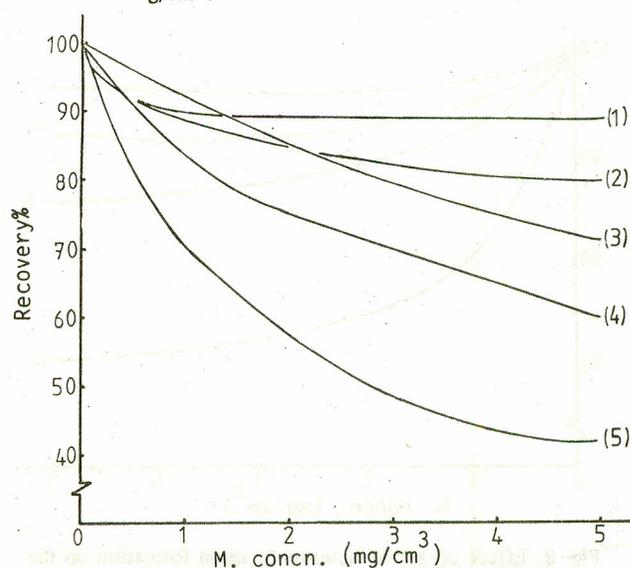


Fig. 7. Effect of $\text{Ge}^*\text{-M}$ heteropoly anion formation on the recovery of $10 \mu\text{g}/\text{cm}^3$ of Mn from 0.1 M hydrochloric acid solution, M = (1) La or Ni, (2) Al or W, (3) Mo, (4) Sc and (5) Sn.
*Ge = $1 \text{ mg}/\text{cm}^3$.

show the general trend which is usually the suppression of the manganese absorption.

Elimination of the heteropoly formations. A series of laboratory synthesized ligands (see Appendix) were prepared and added to the solutions of the analytes where heteropoly centres existed. Fig. 11-13 show the effect of these ligands in eliminating the phenomenal effect on manganese, chromium and nickel absorption respectively. The most effective ligand for the purpose is N-cyanoacyl acetaldehyde hydrazone (L_1). Its application to mixtures of heteropoly centres and the analyte in hydrochloric

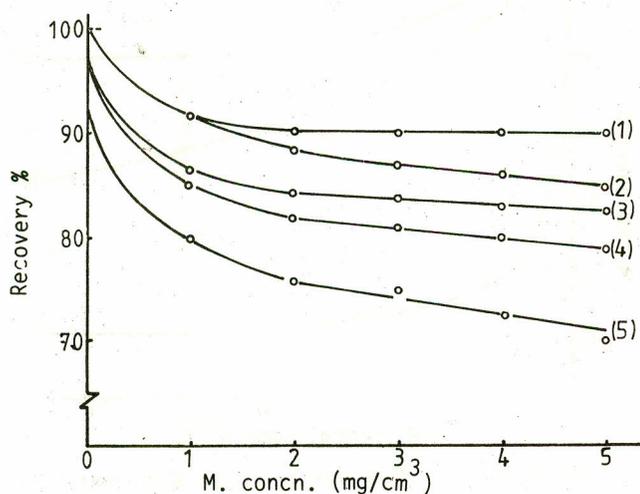


Fig. 8. Effect of V^*-M heteropoly anion formation on the recovery of $10 \mu\text{g}/\text{cm}^3$ of Mn from 0,1 M hydrochloric acid solution, M = (1) La, (2) Al, (3) Ni, (4) Mo and (5) Ge. $*V = 1\text{mg}/\text{cm}^3$.

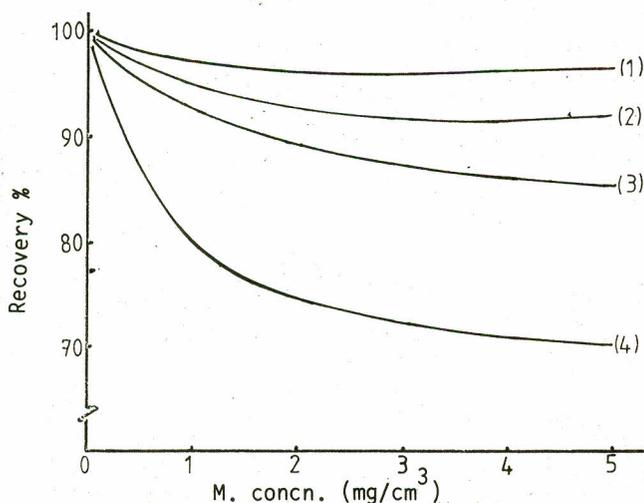


Fig. 9. Effect of As^*-M heteropoly anion formation on the recovery of $10 \mu\text{g}/\text{cm}^3$ of Mn from 0,1 M hydrochloric acid solution, M = (1) W, Cr, Ti, Rh or V, (2) Ge, Sn or Mo, (3) Al and (4) Ni. $*As = 1\text{mg}/\text{cm}^3$.

acid solution restored the recovery of the analyte manganese as indicated in Table 3.

To trace the formed species to elucidate the equilibrium in solution where the analyte manganese, L_1 and the heteropoly centre are found together, the spectrophotometric molar ratio method [13] was followed. The stoichiometry of the probable species was traced and the values of the apparent formation constants are shown in

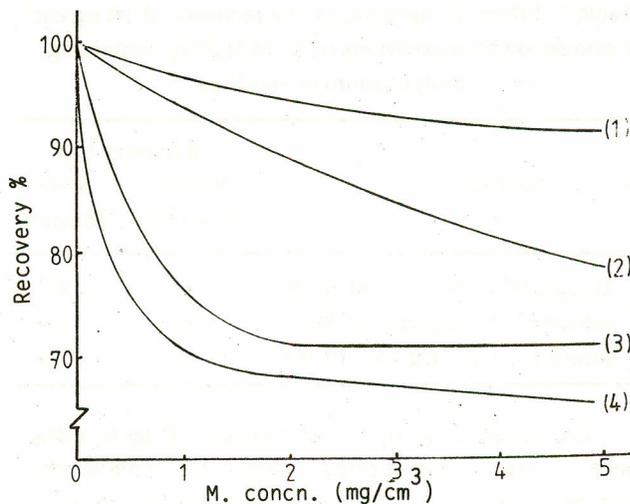


Fig. 10. Effect of Sb^*-M heteropoly anion formation on the recovery of $10 \mu\text{g}/\text{cm}^3$ of Mn from 0,1 M hydrochloric acid solution, M = (1) Rh Ge or Ti, (2) V, Sn, Al, As or Bi, (3) Ni and (4) Mo.

$*Sb = 1\text{mg}/\text{cm}^3$.

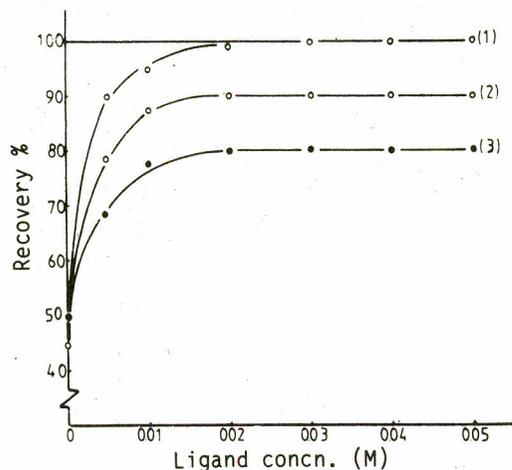


Fig. 11. Recovery of $10 \mu\text{g}/\text{cm}^3$ of Mn in the presence of synthetic ligands to deform phosphomolybdate* or phosphorhodate* ions, (1) Mo or Rh + L_1^{**} , (2) Rh + L_2^{**} , or L_3^{**} and (3) Mo + L_2^{**} , or L_3^{**} .

$*P = 3\text{mg}/\text{cm}^3$, Mo = $10\text{mg}/\text{cm}^3$ and Rh = $0.5\text{mg}/\text{cm}^3$

$L_1 = N\text{-cyanoacyl acetaldehyde hydrazone}$, $L_2 = N\text{-cyanoacyl acetone hydrazone}$ and $L_3 = N\text{-cyanoacyl butyraldehyde hydrazone}$.

Table 4. In all cases, the apparent formation constants of the metal complexes formed in solution decrease in the following order: molybdenum > rhodium, molybdenum > manganese and rhodium > manganese.

Suggested mechanism. It is quite certain that polymeric formations are only constructed as a result of the

Table 3. Recovery percentage of $10 \mu\text{g}/\text{cm}^3$ of manganese from solutions of 0.1M hydrochloric acid containing heteropoly anion centres.

No.	Added cations in 1 mg mg/cm^3 concentration level	Recovery of $10 \mu\text{g}/\text{cm}^3$ of Mn	
		before treatment	after treating with 0.025 M of L_1
1.	Mo	100	100
2.	P* + Mo	50	100
3.	P* + Mo + Al	76	99
4.	P* + Mo + Cd	96	100
5.	P* + Mo + Li	67	100
6.	P* + Mo + Sr	87	99
7.	Rh**	100	100
8.	P* + Rh**	45	100
9.	P* Rh** + Co	55	100
10.	P* + Rh** + Fe + Sn	70	109
11.	Si	100	100
12.	Si + Mo	74	100
13.	Ge	100	100
14.	Ge + Sn	70	90
15.	Ge + Sc	84	95
16.	V	100	100
17.	V + Mo	85	100
18.	As	100	100
19.	As + Al	93	98
20.	Sb	100	100
21.	Sb + Mo	70	100

*3 mg/cm³ of P as phosphoric acid. **Rh = 0.5 mg/cm³.

Table 4. Apparent formation constants of Mn, Mo or Rh - L_1 complexes in solution.

Ligand	Melting point	Metal	Solvent	λ_{max}	Type of complex	Metal conc. (M)	A/A_m	K_f
CN-CH ₂ CONHN=C=	124	Mn	H ₂ O	206	1:1	1×10^{-3}	0.967	10^6
		Mo		350		1×10^{-4}	0.983	3.87×10^7
		Rh		274		1×10^{-3}	0.979	2.2×10^7

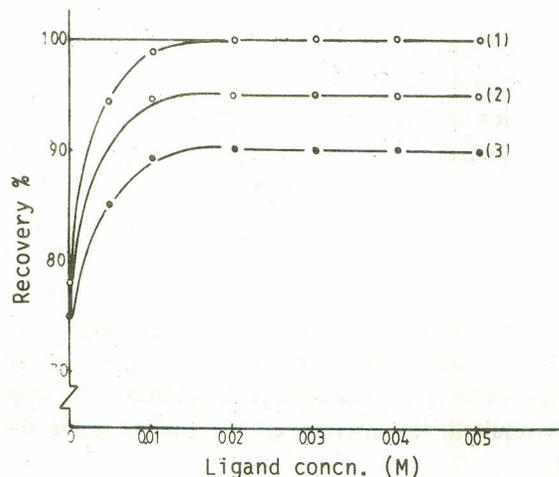


Fig. 12. Recovery of $50 \mu\text{g}/\text{cm}^3$ of Cr in the presence of synthetic ligands to deform phosphomolybdate* or phosphorhodate* ions, (1) Mo or Rh + L_1 , (2) Rh + L_2 , or L_3 and (3) Mo + L_2 or L_3 .
*P = 3 mg/cm³, Mo = 1 mg/cm³, and Rh = 1 mg/cm³.

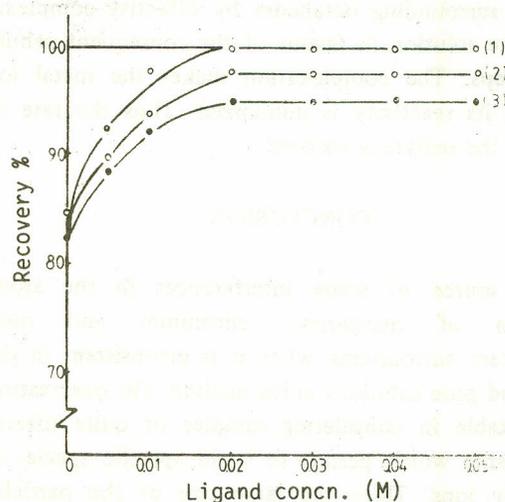


Fig. 13. Recovery of $10 \mu\text{g}/\text{cm}^3$ of Ni in the presence of synthetic ligands to deform phosphomolybdate* or phosphorhodate* ions, (1) Mo or R + L_1 , (2) Rh + or L_3 and (3) Mo + L_2 or L_3 .
*P = 3 mg/cm³, Mo = 1 mg/cm³ and Rh = 1 mg/cm³.

condensation process of definite ions as phosphate and that can occur in solution and do not normally go beyond the formation of the condensed species except when an ion as molybdate or rhodate is present in solution. The latter build into a heteropoly anion. Such equilibrium exists in solution before the process of aspiration commences. During the process of nebulization, dehydration takes place and the heteropoly units are packed together to form crystals with irregular surfaces and large cavities. The irregular surfaces permit the adsorption of the other species including the analyte. In addition, the large cavities result in the insertion of the analyte inside the crystal.

The rate of evaporation of such large particles of compounds occluding the analyte is low compared to the evaporation rate of the analyte particles alone.

When L_1 is added to the solution containing the heteropoly centre, it acts upon the metal ions associated with the surrounding octahedra by effective complexation in the solution in favour of the consequent nebulization steps. The complexation makes the metal ion inert and its reactivity is minimized. Thus the rate of release of the analyte is restored.

CONCLUSION

The source of some interferences in the atomic absorption of manganese, chromium and nickel is the direct surrounding when it is inconsistent in the sample and pure solutions in the analyte. The observation is remarkable in considering samples of quite diverse concomitants which permit to build specific species as heteropoly ions. Thus, the large size of the particles formed delays the release of the analyte in comparison to that of the analyte alone. The deformation of these particles before reaching the flame is essential for the vaporization of the analyte to proceed to completion.

APPENDIX

(a) *Preparation of the ligands.* Two stages were followed to prepare the ligands.

- (b) *Preparation of cyanoacetylhydrazine.* Add dropwise with stirring 25 cm³ of hydrazine hydrate to 65 cm³ of a solution of ethyl cyanoacetate in absolute ethanol. Leave in a refrigerator till cyanoacetylhydrazine separates (≈ 2 hr); filter off and crystallize from ethanol; dry in a vacuum desiccator over anhydrous calcium chloride.
- (c) *Preparation of the hydrazones.* Dissolve 10 g of the cyanoacetylhydrazine in the minimum amount of ethanol, cool, add 5.0, 7.5 or 8.0 cm³ of acetaldehyde, acetone or butyraldehyde to separate L_1 , L_2 or L_3 respectively. Filter off and complete as complete as step a.

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