

Ion chromatographic analysis of inorganic molecular metal–oxygen cluster compounds

A. Jürgensen, G. B. McGarvey and J. B. Moffat*

Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1 (Canada)

ABSTRACT

An ion chromatographic technique for the measurement of the concentrations of metal–oxygen cluster anions and the determination of their elemental compositions has been developed. The method depends on the decomposition of the heteropoly anions into their simpler constituent ions by the addition of a basic hydroxide and the subsequent separation and analyses of these constituent ions. Although the susceptibility of the metal–oxygen cluster anions to decomposition in basic solutions is well known and ion chromatography has been supplied to the analysis of tungstate, molybdate and phosphate ions the application of the former observation and the latter method in combination for the analyses of metal–oxygen cluster anions has not been reported previously. The analytical method described here thus constitutes the first reported application of ion chromatography for the determination of concentration and elemental composition of metal–oxygen cluster anions. The method additionally offers the possibility of application in the study of the mechanism of the synthesis and decomposition of the metal–oxygen cluster anions.

INTRODUCTION

Inorganic molecular metal–oxygen cluster compounds possess interesting structures and unusual properties [1,2] and as a result of the latter have found application in areas as diverse as medicine and heterogeneous catalysis.

The metal–oxygen cluster compounds which have received the greatest attention as heterogeneous catalysts are those frequently referred to as 12-heteropoly oxometalates with anions of Keggin structure. The anion has a tetrahedron (MO_4) at its centre which is enveloped by twelve octahedra (XO_6) and share oxygen atoms to produce a stoichiometry of $[(\text{XO}_4)(\text{M}_{12}\text{O}_{36})]^{n-}$ (Fig. 1).

These heteropoly anions can be found with a wide variety of cations, from the proton itself to relatively large organic species. With the proton as cation, solid acids are formed while with certain of the monovalent cations (*e.g.* NH_4^+) microporous secondary structures are formed [3].

A variety of methods have been employed for the study of metal–oxygen cluster compounds in both

solid and solution form [2]. Electromotive force methods [4] and polarography [5] have been applied for many years and more recently various NMR techniques [6,7] and UV and IR spectroscopy [6]

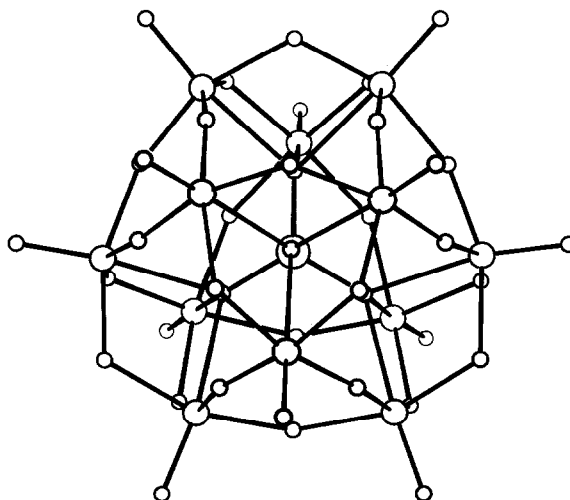


Fig. 1. Heteropoly oxometalate anion of Keggin structure; large circles: central atom (P) and peripheral metal atoms (W or Mo); small circles: oxygen atoms.

have been utilized. Of course X-ray diffractions has for many years been an important tool for structural identification [8]. However, relatively little work has been reported on the application of chromatographic methods, undoubtedly as a consequence of the large size and complex nature of the heteropoly anions. Recently, however, Kirk and Finke [9] have reported the development of a high-performance liquid chromatographic method for the separation of highly charged polyoxometalates which promises to have considerable value in analytical applications.

The present work is concerned with the analysis of the 12-heteropoly anions of Keggin structure by the use of ion chromatography. Although it is possible, in principle, to analyze these as discrete entities by ion chromatography, for various reasons including their size and relative instability in the presence of bases, it seems preferable to decompose these into their smaller constituent ions and analyze for the latter.

The structural instability of the metal-oxygen cluster anions in basic solutions is well known and, in general, the oxyanion products of the decomposition have been identified. Further, ion chromatographic methods are available for the separation and analyses of their constituent oxyanions such as phosphates, molybdates and tungstates. However, there are no reports of the use of the decomposition of the metal-oxygen cluster anions in combination with the ion chromatographic analyses of the decomposition products as a technique for the determination of the concentration of these cluster anions. The present work demonstrates the validity of this method not only for the determination of the concentrations of the metal-oxygen cluster anions but also as a means of obtaining the elemental compositions of the cluster anions. Consequently the present method appears to be superior to one involving the analyses of the cluster anions as discrete entities. Further, as will become apparent subsequently, the technique offers interesting possibilities for the study of the mechanism of the preparation and decomposition of these anions.

The variables of importance thus are of two kinds, those involved with the chemistry related to the decomposition of the heteropoly anions, and those relating to the separation of the constituent species on the chromatographic column.

EXPERIMENTAL

Cation and heteropoly anion analyses were made with a Dionex series 4500i ion chromatograph equipped with a conductivity detector. Cation analyses used the Dionex Fast cation separation columns and an eluent consisting of 20 mM HCl and 0.3 mM 2,3-diaminopropionic acid monohydrochloride (DAP). Background conductivity suppression was achieved using a Dionex cation micromembrane suppressor column and the closed loop Autoregen system with 0.1 M tetrabutylammonium hydroxide as the regenerant. Chromatograms were recorded on a Spectra-Physics ChromJet integrator.

Anion chromatography employed a Dionex AG5 guard column and AS5 separator column with a 10 mM NaCO₃-10 mM NaOH eluent. The background conductivity was reduced using an anion micromembrane suppressor column with a 30 mM H₂SO₄ regenerant.

The present report focuses on 12-tungstophosphoric and 12-molybdophosphoric acids and their salts of monovalent cations. Thus, for the anion analyses potassium phosphate (Baker), sodium molybdate (BDH) and sodium tungstate (Aldrich) were employed for calibration purposes. These were dried at 110°C and stored in a desiccator prior to use. Aqueous solutions of accurately known concentrations were prepared from triply distilled deionized water. In order to avoid saturation of the ion chromatography columns all solutions were carefully diluted to concentrations in the 0-10 ppm range.

Aqueous solutions each containing two anionic components, namely phosphate and molybdate or the former and tungstate were prepared in order to provide an independent confirmation of the calibrations.

Finally, aqueous solutions of known concentration of the heteropoly oxometalate were treated with an aqueous solution of either lithium or sodium hydroxide to decompose the heteropoly anion and were then subjected to analysis.

RESULTS AND DISCUSSION

Data obtained in the calibration for the phosphate, molybdate and tungstate ions were fitted to a polynomial the coefficients and the standard devia-

TABLE I
CALIBRATIONS: POLYNOMIAL^a COEFFICIENTS AND
STANDARD DEVIATIONS

Anion	Coefficients				S.D. ($\times 10^4$)
	<i>a</i> ($\times 10^5$)	<i>b</i> ($\times 10^4$)	<i>c</i> ($\times 10^2$)	<i>d</i> ($\times 10^4$)	
PO ₄ ³⁻	-7.28	-5.35	3.97	31.15	9.48
MoO ₄ ²⁻	0.104	-0.384	2.12	8.47	35.4
WO ₄ ²⁻	-1.84	8.56	2.03	-13.57	27.15

$$^a y = ax^3 + bx^2 + cx + d$$

tions for which are shown in Table I. Retention times of approximately 4.4, 5.1 and 8.9 min for tungstate, molybdate and phosphate ions were obtained under the present operating conditions. The phosphate graph is linear up to a concentration of 0.12 mmol/l. The molybdate and tungstate calibration curves on the other hand, show two distinct linear ranges over the concentration range considered. It is interesting to note the differences in the detector response to the three species considered in the present study. Whereas the response for the phosphate was *ca.* 230 arbitrary units/(mmol/l), the response for the transition species was much lower. For the molybdate calibration curve, the response factor below 0.6 mmol/l was *ca.* 50 but at the highest measured concentrations this value fell to 46. More dramatic concentration effects were observed for the tungstate calibration. Two distinct regions were observed: one below 0.12 mmol/l with a response factor of 41, and one at higher concentrations with a response factor of 37.

The large differences in the response factors can be explained in part by the ionic mobility of the anions. The size, charge distribution, and concentration of the anion will be the factors that most strongly influence the response characteristics. While the formal charge of the three species is the same (-2) the sizes of the ions vary as indicated by the metal atom-oxygen bond lengths of 1.54, 1.76 and 1.79 Å for HPO₄²⁻, MoO₄²⁻, and WO₄²⁻ respectively. The larger size of the transition metal oxyanions presumably leads to a smaller charge density and reduced mobility and hence a lower detector response. The differences between the response factors of the two transition metal species is not readily

explained although the additional f-shell electrons in the tungstate ion are expected to exert an influence.

In order to provide independent tests of the calibration, aqueous solutions containing two ionic species, either the phosphate and the molybdate or the phosphate and the tungstate anions were prepared. After suitable dilution to concentrations within the range of calibration, aliquots were passed through the ion chromatograph and concentrations of the two components were obtained from the peak areas and the calibration plots. The measured concentrations of phosphate and molybdate and of phosphate and tungstate in solutions containing the former or latter pair of species were compared with the expected concentrations from the preparation. The coefficients for the linear equation employed to fit the data from the analysis of solutions containing known concentrations of each of two anions are shown, together with the standard deviation, in Table II. The measured concentrations are in good agreement with the expected values. It is evident that suitable precision is attainable provided that changes in the detector response as a function of concentrations are taken into account.

As pointed out in the introduction the analyses of the heteropoly oxometalates are based on the preliminary decomposition of the heteropoly anion in aqueous solution followed by the separation and analysis of the constituent ions by ion chromatography. Although the heteropoly anions are unstable with respect to this decomposition process in basic solutions, the range of pH within which the 12-het-

TABLE II
LINEAR EQUATION^a COEFFICIENTS AND STANDARD
DEVIATIONS FROM CALIBRATION TESTS WITH TWO
ANION COMPONENT SOLUTIONS

Analysis anion	Second anion	Coefficients		S.D. ($\times 10^3$)
		<i>a</i>	<i>b</i> ($\times 10^3$)	
PO ₄ ³⁻	WO ₄ ²⁻	0.988	1.12	1.52
PO ₄ ³⁻	MoO ₄ ²⁻	0.966	0.70	2.28
WO ₄ ²⁻	PO ₄ ³⁻	0.974	1.11	4.84
MoO ₄ ²⁻	PO ₄ ³⁻	0.998	-3.88	5.92

$$^a y = ax + b$$

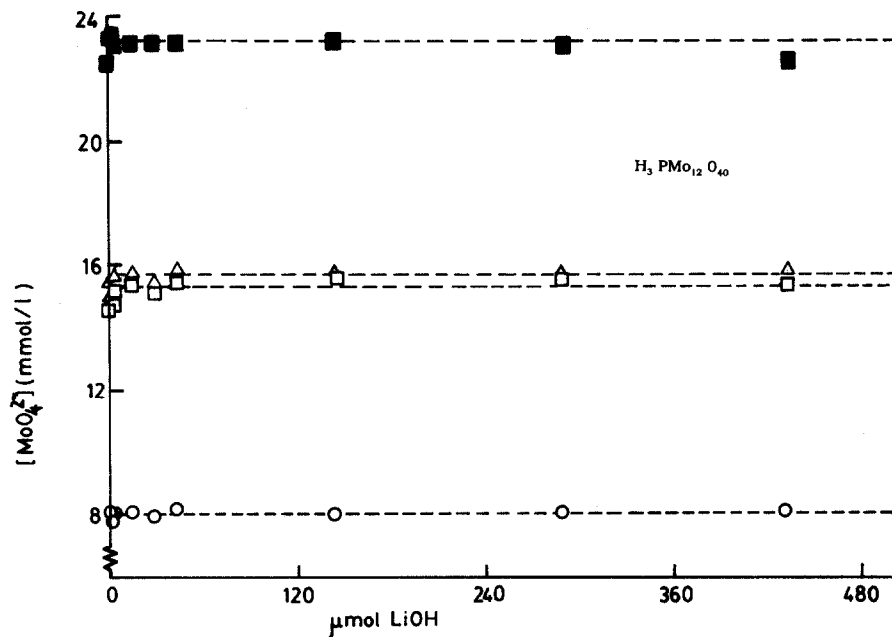


Fig. 2. Measured concentrations of molybdate ions from aqueous solutions of 12-molybdophosphoric acid after addition of lithium hydroxide. (Dashed lines are expected quantities.) Expected concentrations: ■ = 23.21 mmol/l; △ = 15.74 mmol/l; □ = 15.36 mmol/l; ○ = 8.03 mmol/l.

eropoly structure is retained intact is dependent upon the nature of both the central and peripheral atoms [10]. Measurements of the ^{31}P chemical shifts of the major species present in aqueous solutions of the two heteropoly anions considered here have shown that for each of the two 12-heteropoly anions, the saturated Keggin anion was found to exist as the single constituent species only in strongly acidic solutions of pH less than 2. At higher solution pH degradation of the Keggin anion to lacunary species was observed as indicated by the large changes in the measured chemical shifts. Only after strongly alkaline conditions were reached was the complete degradation of the Keggin anion to simple oxyanions assured.

In the present work hydroxides have been employed as convenient and non-interfering bases for purposes of affecting the decomposition of the heteropoly anions. To evaluate the influence of the cation in the base, lithium and sodium hydroxides were separately employed. A number of aqueous solutions of 12-molybdophosphoric acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) and of 12-tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) were prepared, the base added and

analyses were performed. Typical results for 12-molybdophosphoric acid and lithium hydroxide are shown in Fig. 2. Although not shown the expected results are obtained with addition of relatively small quantities of either base.

Further, addition of much larger quantities of either base has no effect on the analytical results. With either alkali the measured concentration of molybdate is in good agreement with that expected from complete decomposition of the heteropoly anion. It should be noted that the results for four separate and distinct solutions of 12-molybdophosphoric acid are shown in Fig. 2. The facile decomposition of the 12-molybdophosphate anion following small additions of either hydroxide confirm the previous reports of the relative instability of this anion in aqueous solutions [2].

Aqueous solutions of 12-tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) were prepared, base was added and analyses were performed. The results with lithium hydroxide are reported in Fig. 3. The differences between the molybdenum and tungsten-containing acids are clearly evident from a comparison of this figure with Fig. 2. With both LiOH and NaOH and

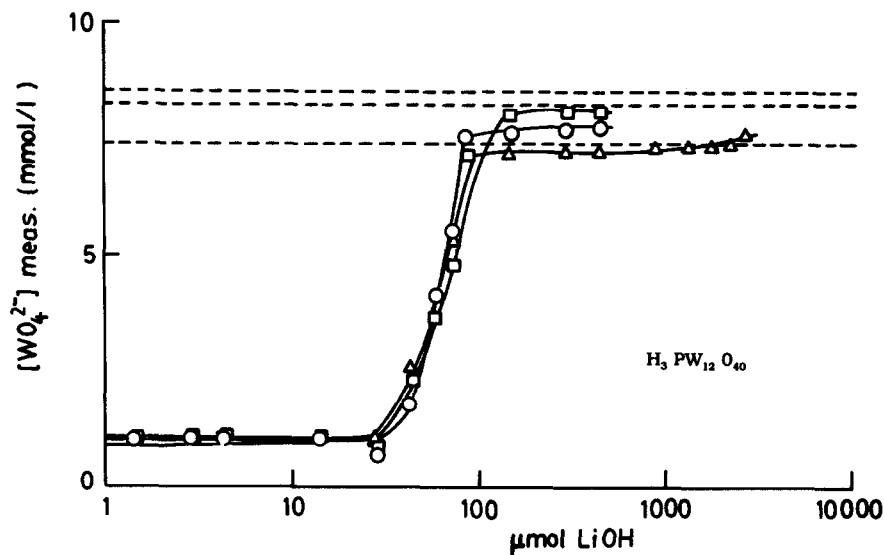


Fig. 3. Measured concentrations of tungstate ions from aqueous solutions of 12-tungstophosphoric acid after addition of lithium hydroxide. (Dashed lines are expected quantities.) Expected concentrations: \square = 8.57 mmol/l; \circ = 8.30 mmol/l; \triangle = 7.44 mmol/l.

the tungsten-containing acid the quantities of tungstate ion measured remain relatively constant as the base is added up to approximately 30 μmol . The small quantity of tungstate detected in the solutions containing the smallest quantities of base suggest that some decapping of the Keggin anion has occurred with subsequent formation of the lacunary species. As the base concentration increases, the increase in the measured quantity of tungstate indicates further decomposition of the lacunary anion to the constituent anions. Finally for the highest quantities of base, the measured tungstate concentrations approach the expected values.

It is clear from the foregoing that the anion of the tungsten-containing heteropoly acid is more resistant to changes in pH than that of the molybdenum-containing acid. Thus, the Keggin structure of the anion of the former acid is retained over a wider range of pH than that of the latter. This is consistent with the results obtained from the earlier NMR studies [10].

The ion chromatographic method for analysis of the metal-oxygen cluster compounds through decomposition to their constituent ions is evidently a versatile method which promises to have applicability to a wide variety of elementary compositions of these solids. It is important to note that the pres-

ent method not only permits the measurement of the concentration of the metal-oxygen cluster anions but in addition provides information on the elemental composition of these anions. Equally interesting and valuable, however, is the ancillary information obtainable from the method on the structural stability of the cluster anions, a subject of considerable importance in this area of chemistry.

CONCLUSIONS

A method has been developed for the analysis of metal-oxygen cluster anions containing a single peripheral metal element, although in principle it is capable of extension to diperipheral cluster anions. The present technique offers the advantage of generating two sets of information, the concentration as well as the elemental composition of the anion. Further, the method has applicability to studies of the mechanism of the synthesis and decomposition of the cluster anions.

ACKNOWLEDGEMENT

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

REFERENCES

- 1 M. T. Pope, A. Müller, *Angew. Chem., Int. Ed. Eng.*, 30 (1991) 34.
- 2 M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, 1983.
- 3 J. B. Moffat, *J. Mol. Catal.*, 52 (1989) 169.
- 4 L. G. Sillen, *Quart. Rev. Chem. Soc.*, 13 (1959) 146.
- 5 P. Souchay, *Ann. Chim.*, 19 (1943) 102.
- 6 L. P. Tsiganok, *Polyhedron*, 8 (1989) 2739.
- 7 G. Chidichimo, *J. Phys. Chem.*, 94 (1990) 6826.
- 8 H. T. Evans, Jr., *Perspec. Struct. Chem.*, 4 (1971) 1.
- 9 A. D. Kirk and R. G. Finke, *Inorg. Chem.*, 28 (1989) 792.
- 10 G. B. McGarvey and J. B. Moffat, *J. Mol. Catal.*, 69 (1991) 137.