Translated from *Uspekhi Khimii*, **46**, 740-749 (1977) U.D.C. 543.544 : 541.49

Gas-chromatographic Analysis of Metals as Volatile Complexes

D.N.Sokolov

The use of gas-chromatographic methods for analysing metals is considered. Attention is paid mainly to study of the gas-chromatographic properties of compounds of metals with various derivatives of β-diketones as well as complexes with thioketones and derivatives of β-ketoimines. Attempts to separate the rare-earth metals gas-chromatographically are examined, together with highly sensitive gas-chromatographic methods for determining traces of metals (beryllium, aluminium, chromium, etc.). A list of 78 references is included.

CONTENTS

I. Introduction 388
II. Complexes with β-diketones 388
III. Volatile complexes with ligands containing oxygen together with sulphur and with nitrogen 390
IV. Other volatile metal compounds 390
V. Gas-chromatographic analysis of traces of metals 391
VI. Behaviour of metal chelates in a chromatographic column 391

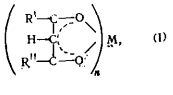
I. INTRODUCTION

During the period covered by the Review, from the end of 1970 to the beginning of 1975, more than seventy publications appeared on the gas chromatography of volatile compounds of metals, including several reviews[1-7] and one monograph[8]. Certain changes in the general approach to the problem have been noticeable during the past five years. Whereas before 1970 the studies in this field were often in the nature of preliminary investigations, the possibilities of the method have now become clear, and the aims more definite. Most of the papers report comparative investigations of the chromatographic properties of volatile complexes of metals having a common feature (usually either complexes of a series of metals with the same ligand or, in contrast, of a series of ligands with the same metal). The authors have usually tried to find either new volatile complexes, with better properties, of metals that have already been chromatographed, or volatile compounds of metals that had previously proved impossible to chromatograph. Thermogravimetric analysis is widely used to assess the volatility of complexes. Papers on the gas-chromatographic separation of rare-earth metals form a special group. The number of papers on the practical application of the gas chromatography of chelates to the determination of traces of such metals as beryllium, aluminium, chromium, etc. has increased. Finally, a few studies have been made on the specific behaviour of metal chelates in chromatographic columns.

II. COMPLEXES WITH β-DIKETONES

1. Simple β-Diketonates

Many papers have appeared on the further study of metal β-diketonates of the type

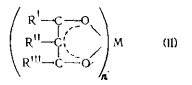


(I)

where n is the charge on the metal ion. The list of complexes investigated has expanded appreciably during recent years. The interest of research workers in the hitherto popular derivatives of hexafluoropentane-2,4-dione and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione diminished somewhat, after which the number of investigations on non-fluorinated β-diketonates increased, especially on derivatives of 2,2,6,6-tetramethylheptane-3,5-dione (dipivaloylmethane) $CH_3.C(CH_3)_2.CO.CH_2.CO.C(CH_3)_2.CH_3$. Thermogravimetric analysis has been used[9,10] to study the volatility and investigate the chromatographic behaviour of chelates of this dione with twenty-five metals, including rare-earth elements, nickel(II), cobalt(II), and zinc(II). In a long paper on the investigation of complexes of chromium(III), aluminium(III), iron(III), palladium(II), copper(II), nickel(II), zirconium(IV), rare-earth metals, uranyl(II), and thorium(IV) with various β-diketones, Kuwamoto[11] also paid great attention to chelates with this dione. In particular, thermogravimetric analysis showed that only neodymium(III) and zirconium(IV) among the above metals, as well as sodium, give chelates that decompose partly on sublimation: all the remaining chelates sublime without decomposition. Numerous chelates of metals with pentane-2,4-dione, its hexa- and tri-fluoro-derivatives, and other β-diketones were also studied. The first chromatogram of a zinc(II) chelate with the above tetramethylheptanedione was reported in this paper.

Investigations on the gas-chromatographic properties of complexes of beryllium, aluminium, scandium, vanadyl(II), chromium(III), iron(III), copper(II), and manganese(II) with 1-thienyltrifluorobutane-1,3-dione[12] and of beryllium, aluminium, iron(III), indium, chromium(III), cobalt(III), thorium(IV), and several rare-earth elements with trifluoro-5,5-dimethylhexane-2,4-dione[13] in the main merely confirmed already known laws and gave no fundamentally novel results, apart from the first chromatogram of a chelate of cerium(IV) with the latter dione[13]. The same applies to a detailed examination[14] of chelates of aluminium, gallium, and indium with pentane-2,4-dione and its alkyl derivatives, hexafluoropentane-2,4-dione, 1-phenyltrifluorobutane-1,3-dione, 1-furyltrifluorobutane-1,3-dione, and 1-thienyltrifluorobutane-1,3-dione. The chromatographic behaviour of chelates of several metals—in particular

beryllium, aluminium, chromium, and copper—with alkylated β-diketones of the type



(II)

has been investigated for the first time [11,14,15]. Unfortunately, the replacement of hydrogen by any alkyl as R'' lowers the volatility of the complex and thereby impairs its gas-chromatographic properties, since there is evidently no accompanying improvement in thermal stability. The introduction of fluorinated radicals as R'' might have given more interesting results, but such chelates have not yet been investigated.

2. Complexes with Mixed Ligands

Recent years have seen a considerable increase in the number of gas-chromatographic studies of mixed-ligand metal complexes, fluorinated β-diketonates containing also one or two molecules of neutral donors such as dimethylformamide (DMF), dimethyl sulphoxide (DMSO), tributyl phosphate (TBP), diethylamine, etc. The gas-chromatographic behaviour of complexes of nickel(II) and cobalt(II) with trifluoropentane-2,4-dione and dimethylformamide having the composition $ML_2.2DMF$ (where L is a singly charged ligand anion) has been investigated [16]. Quantitative determination of each complex to 0.2 mg proved possible, with separation effected at a relatively low temperature (100°C). The gas chromatography of volatile mixed complexes of zinc $ZnL_2.A$ (where A is a molecule of tri-n-butyl phosphate or tri-n-butylphosphine oxide—TBPO) has also been described [17]. Furthermore, the same paper reported the gas-chromatographic behaviour of mixed chelates of zinc with trifluoropentane-2,4-dione and 4-methylpyridine and with pentane-2,4-dione and 2,2'-bipyridyl. The best results were obtained with the chelate having the composition $ZnL_2.TBPO$.

Investigations have been made on mixed complexes $UO_2L_2.DBSO$ and $ThL_4.DBSO$ formed by uranyl and thorium(IV) with hexafluoropentane-2,4-dione and dibutyl sulphoxide [11] and on complexes of analogous composition with 1,1,1,2,2,6,6,7,7,7-decafluoroheptane-3,5-dione, hexafluoropentane-2,4-dione, and trifluoropentane-2,4-dione with neutral donors (dibutyl sulphoxide, tributyl phosphate, and tributylphosphine oxide). [18] The best results were obtained with hexafluoropentanedione and dibutyl sulphoxide: use of these complexes enabled uranium and thallium at concentrations of 1–120 g litre^{-1} to be determined in solutions with a relative error $< 10\%$. The limiting dilutions for uranium and thorium were respectively 0.6 and 0.4 g litre^{-1}.

Jacquelot and Thomas [19] chromatographed mixed complexes $ML_2.2(C_2H_5)_2NH$ of nickel(II) and cobalt(II) with 1-thienyltrifluorobutane-1,3-dione and diethylamine, but the form of the peaks left much to be desired. Furthermore, nickel and cobalt could not be separated, since the two complexes had almost the same retention times. It is interesting that these workers treated the solid carrier with potassium hydroxide to improve the chromatogram. This was probably the first use of this procedure in the gas chromatography of metal chelates.

The properties of complexes of iron(II) and iron(III) with hexafluoropentanedione and tributyl phosphate, as well as their chromatographic behaviour, have been examined in detail [20]. Iron(II) forms a complex $FeL_2.2TBP$, while iron(III) yields FeL_3 and $FeL_3.TBP$, with in the latter case one of the hexafluoropentanedione anions (L^-) acting as a unidentate ligand. During chromatography the compound $FeL_2.2TBP$ dissociates in the gas phase, but iron(III) present in the complex $FeL_3.TBP$ is reduced in the chromatographic column to iron(II).

Burgett [21] has studied the gas-chromatographic behaviour of complexes $ML_2.2DBSO$ of iron(II), cobalt(II), and nickel(II) with decafluoroheptanedione. He includes results for the chromatographic behaviour of the copper chelate CuL_2 with the same ligand. The ion Cu^{2+} does not form complexes having mixed ligands. In the chromatography of small quantities the form of the peaks of all the complexes studied was distorted. The peak of the copper chelate changed form also in the presence of mixed complexes of nickel(II) and cobalt(II).

3. Binary Complexes

Studies have been made not only on complexes having mixed ligands but also on volatile binary complexes, which contain more than one identical ligand and ions of two different metals. The latter complexes are usually formed only from fluorinated β-diketones. Belcher et al. [22] showed that, in the presence of excess of the ligand, chelates ML_3 of rare-earth metals with fluorinated β-diketones react with alkali-metal cations M' to form complexes $M'ML_4$. The products sublimed in a vacuum without decomposition, but evidently could not be used for gas chromatography. Gurevich et al. [23] prepared volatile complexes $M'CoL_3$ (in which $M' = K^+$, Rb^+, Cs^+, while L represents a hexafluoropentanedione anion), obtained chromatograms of individual compounds, and effected the gas-chromatographic separation of potassium and rubidium complexes on a stainless-steel column 200 × 0.1 cm containing 1% of Silicone SE-30 on Chromaton N at 250°C. It is interesting that retention of the binary complexes diminished in the sequence from potassium through rubidium to caesium. No mention was made [23] of the possibility of using the resulting complexes for quantitative analysis.

4. Separation of Rare-earth Metals

The excellent results obtained when gas chromatography is used to separate compounds of closely similar properties naturally suggest the possible application of this method to solve one of the most difficult problems of analytical chemistry, separation of the rare-earth metals. Volatile complexes of these elements with dipivaloylmethane suitable for use in gas chromatography were first prepared in 1965. [24] Since then researches on the gas-chromatographic properties of various volatile rare-earth β-diketonates have been published regularly, but significant progress in this field has evidently not yet been made. Japanese workers have been responsible for the largest number of papers on the gas chromatography of the rare-earth metals; they have studied complexes with tetramethylheptane-3,5-dione [9-11,25,26], trifluorodimethylhexane-2,4-dione [13], and the latter together with a neutral donor (tributyl phosphate or tri-n-octylphosphine oxide) [27]. Interesting papers on the gas chromatography of mixed-ligand complexes of rare-earth metals have been published by Burgett and Fritz [28-30] and by Sieck and Banks [31].

However, the main task—complete separation of the whole group of rare-earth metals—remains unsolved. Only one case of the separation of chelates of two neighbouring rare-earth metals (complexes of europium and

samarium with dipivaloylmethane)[22], on a column of 2% of a fluorinated silicone oil on Chromosorb G only 45 cm long with temperature programming has been reported. This work was published in 1969, but other workers have evidently been unable to repeat the separation, and publications during recent years represent in most cases the chromatograms of rare-earth metals taken singly, but in some cases as mixtures of two or three elements[25,27-29,31].

Comparison of papers by the same group of workers over several years (1968–1972) shows that the use of complexes with various β-diketones has not yielded any significant improvement in the separation of rare-earth metals[26,27,32]. Recently several investigators have again returned to the study of the dipivaloylmethane complexes, but without especial success[9,10,25]. It is stated[9,10] that a most efficient column is required for the separation of a mixture of lutetium and ytterbium chelates (> 11 000 theoretical plates), whereas 650 theoretical plates are sufficient to separate neodymium and praseodymium chelates. However, despite the availability of such an inefficient column, no attempt was made to achieve even this separation, undoubtedly owing to the additional difficulties encountered in solving the problem. In particular, attempts to improve the efficiency of separation of rare-earth chelates by lengthening the column resulted in broadening of the peaks, so that the separation not only did not improve but even deteriorated. According to other workers[29] the optimum column length is ~ 50 cm. This is probably why columns not longer than 70–75 cm have been used in most attempts at the separation of rare-earth complexes[13,25-27].

III. VOLATILE COMPLEXES WITH LIGANDS CONTAINING OXYGEN TOGETHER WITH SULPHUR AND WITH NITROGEN

1. Derivatives of 4-Thionopentan-2-one

The first research on the gas chromatography of volatile chelates of metals with thioacetylacetone—a ligand containing oxygen and sulphur as donors $CH_3.CS.CH_2.CO.CH_3$—was undertaken by Stephen et al.[33] in 1969. Investigations on these lines have since been continued. In a detailed examination of bivalent compounds of nickel, zinc, cadmium, lead, palladium, platinum, and cobalt with thioacetylacetone Belcher et al.[34,35] found that most of them are monomeric ML_2, in contrast to the complexes of these metals with β-diketones, which in most cases are polymeric or hydrated. These workers established that the volatility of the chelates diminished in the sequence

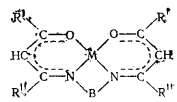
$$\text{nickel} > \text{zinc} > \text{cobalt} > \text{palladium}$$

where only the nickel(II) chelate vaporised completely without decomposition. However, even it was unsuitable for the gas-chromatographic determination of small quantities of the metal. Considerably better gas-chromatographic properties were observed in chelates of several bivalent metals with fluorinated derivatives, e.g. trifluoro-4-thionopentan-2-one[35-37]. Thus chelates of the latter with nickel(II), zinc(II), and cobalt(II) sublimed completely, and those with palladium(II) and platinum(II) by 85% and 65% respectively[36]. These workers were able to separate the nickel, palladium, and platinum chelates on a column comprising 2.5% of Apiezon L on Universal B at 170°C. In a later study[38] the same workers used the nickel(II) complex of trifluorothioacetylacetone for the gas-chromatographic determination of traces of nickel (down to 5×10^{-11} g) in alloys, tea, and fats using an electron-capture detector.

Bayer et al.[39,40] investigated the gas-chromatographic behaviour of chelates of nickel(II), palladium(II), and platinum(II) with another sulphur-containing ligand, hexafluoro-4-thionopentan-2-one. The resulting chelates were far more volatile than those with the trifluoro-derivative, and their gas-chromatographic separation was achieved on columns with 1% of SE-30 and with 3% of OV-17 on Chromosorb W at only 80°C. It is interesting that many metals that form very stable chelates with β-diketones (beryllium, aluminium, chromium, etc.) do not react at all with fluorinated β-thioketones such as trifluorothioacetylacetone.

2. β-Ketoiminates

The first paper on the gas chromatography of volatile β-ketoiminates of copper(II) and nickel(II) was published in 1967.[41] Since 1971 several interesting studies have appeared by Belcher, Uden, et al.[42-47] Especially promising results were obtained for the bivalent nickel, copper, palladium, and platinum complexes with quadridentate β-ketoimines



where B = $[CH_2]_2$, $[CH_2]_3$, or $CH_2.CH(CH_3)$, R′ = CH_3, and R″ = CH_3 or CF_3. The vapour pressure of such chelates is low, and they had to be chromatographed at high temperatures (up to 250°C), but their thermal stability resulted in almost complete absence of decomposition in the column.

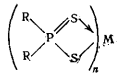
Comparative studies on complexes of copper(II) and nickel(II) with bi- and quadri-dentate β-ketoimines showed that the gas-chromatographic behaviour of the latter was to be preferred, especially in the chromatography of small quantities of the complexes. In particular, the gas-chromatographic determination of copper and nickel in quantities down to 10^{-13} g was achieved[46,47]. An interesting fact was revealed by examination of the chelates of these metals with quadridentate ligands containing oxygen and nitrogen. The replacement of terminal alkyl by perfluoroalkyl groups in β-diketones leads in all known cases to an increase in the vapour pressure of the corresponding metal chelates, a rule which is satisfied also for bidentate β-ketoiminates. With quadridentate β-ketoimine complexes (the bivalent copper and nickel complexes were investigated), however, the opposite relation is unexpectedly observed: i.e. the introduction of terminal trifluoromethyl groups into the ligand does not increase but lowers the volatility of the copper(II) and nickel(II) β-ketoiminates[46,47]. No explanation has yet been found for this fact.

IV. OTHER VOLATILE METAL COMPOUNDS

In 1969 D'Ascenzo and Wendlandt[48] suggested that the gas chromatography of copper, nickel, and zinc could be effected by use of the diethyldithiocarbamates, supposedly possessing adequate volatility. When tested, however, this suggestion proved unfortunate, and was rejected[49]. Barratt et al.,[50] examined the suitability for gas chromatography of volatile beryllium and zinc hydroxyacetates and hydroxypropionates M_4OR_6, where R = CH_3COO^- or $C_2H_5COO^-$. They were able to separate the beryllium and

zinc complexes on a glass column with 5% of Apiezon L on Universal B at 150°C. However, the chromatographic properties of the compounds leave much to be desired.

Kleinmann and Neeb[51] chromatographed complexes of gold(I), cadmium(II), and zinc(II) with dialkyldithiophosphines



where R = CH_3, C_2H_5, and C_3H_7. They were able to obtain peaks of the individual complexes and to separate the diethyl-, dipropyl-, and dibutyl-dithiophosphinate complexes of zinc(II) on a glass column with 3% of Silicone OV-225 on Chromosorb W at 220°C. From the form of the peaks the gas-chromatographic properties of these chelates are apparently also far from ideal. Nevertheless, the chromatogram obtained is interesting in demonstrating the kinetic stability of the zinc complexes: otherwise, the chromatogram would have indicated the presence of mixed complexes formed by ligand exchange.

The possibility of the gas-chromatographic determination of certain metals as volatile trimethylsilyl derivatives of anions containing the metal is of interest. Thus a paper on the gas-chromatographic analysis of anions[52] mentions among others the possible determination of the vanadate ion VO_3^-. Since many metals—aluminium, chromium, manganese, niobium, tantalum, molybdenum, tungsten, bismuth, lead, tin, etc.—may occur as anions, this raises the hope that new methods may appear for the gas-chromatographic analysis of metals.

Finally, we must note the possibilities that have appeared for the quantitative determination of metals as volatile organometallic compounds. Such compounds had hitherto been regarded as of little interest for the gas-chromatographic analysis of metals, since in most cases quantitative conversion of the metal into the compound could not be achieved. Recently, however, exceptions have appeared to this rule. The first such work was published in 1968 by Bock and Monerjan on the determination of thallium as its cyclopentadienyl derivative[53]. However, as yet this is the only publication on the use of cyclopentadiene derivative in this way. Two interesting papers have appeared on the gas chromatography of several elements—thallium, selenium, tellurium, mercury, arsenic, antimony, bismuth, and tin—as their phenyl derivatives $(C_6H_5)_nM$.[54,55] It is very important that phenyl derivatives of all the above elements (other than thallium) are readily obtained quantitatively by the reaction of phenylmagnesium bromide with diethyldithiocarbamates of the metals in absolute ether. The phenyl derivatives of selenium, tellurium, mercury, arsenic, antimony, and bismuth were separated on a column comprising 5% of Carbowax 20M with added terephthalic acid on Gasochrome Q with a programmed temperature rise from 180 to 220°C (10 deg min^{-1}), and also those of thallium, selenium, and tellurium on a column with 3% of Silicone OV-17 on Gasochrome Q under isothermal conditions at 160°C. Further research on these lines may lead to the development of quantitative gas-chromatographic methods of analysis for the above and other elements.

V. GAS-CHROMATOGRAPHIC ANALYSIS OF TRACES OF METALS

The chief practical value of the gas-chromatographic analysis of volatile compounds of metals consists in the high sensitivity attainable in the determination of chelates of several metals by means of such devices as an electron-capture detector or a microwave emission detector. Gas-chromatographic analysis is comparable in sensitivity with such highly sensitive methods as neutron-activation analysis, mass spectrometry with a spark source, and flameless atomic-absorption spectroscopy, sometimes even surpassing them.

During recent years several papers have been published on the practical application of the gas-chromatographic determination of traces of certain metals as volatile chelates. Descriptions have appeared of the gas-chromatographic determination of beryllium in air[56], terrestrial and lunar rocks and meteorites[57], in the leaves of trees[58], and in various biological materials[59,60], aluminium and chromium in uranium[61], aluminium in sea-water[62] and in polymers[63], nickel in alloys, tea, and fats[38], nickel and copper in biological materials[46], cobalt in vitamin B_{12},[64] and chromium in aqueous solutions[65] and in various biological materials[66-69]. Chelates with trifluoropentane-2,4-dione have been most widely used, but other complexes have also found application[38,46,63,64].

Use of volatile complexes of metals in analysis of traces of elements.

Element	Ligand	10^{10} x Limit of detection, g	Ref.
Al	trifluoropentane-2,4-dione	0,009	63
	trifluoro-5,5-dimethylhexane-2,4-dione	0,04	63
As	phenyl	4	54
Be	trifluoropentane-2,4-dione	0,0004	57
Co	heptafluoro-7,7-dimethyloctane-4,6-dione	0,4	64
Cr	trifluoropentane-2,4-dione	0,0025	68
	pentane-2,4-dione	0,03	71
Cu	trifluoropentane-2,4-dione	0,08	71
	quadridentate β-ketoimines	0,001	46
Fe	trifluoropentane-2,4-dione	0,13	71
Ga	trifluoropentane-2,4-dione	0,027	71
Ni	trifluoro-4-thionopentan-2-one	0,5	38
	quadridentate β-ketoimines	0,007	46
Pd	trifluoro-4-thionopentan-2-one	2 000	36
Pt	trifluoro-4-thionopentan-2-one	3 600	36
Sc	pentane-2,4-dione	0,021	71
	trifluoropentane-2,4-dione	0,03	71
Th	hexafluoropentane-2,4-dione + tributylphosphine oxide	8 000	18
Tl	cyclopentadiene	10 000	53
U	hexafluoropentane-2,4-dione + tributylphosphine oxide	12 000	18
V	trifluoropentane-2,4-dione	0,085	71
Rare-earth metals	decafluoroheptane-3,5-dione + dibutyl sulphoxide	200—300	28

Highly sensitive devices other than the electron-capture detector are beginning to be used for the determination of microquantities of chelates, including mass-spectrometric[70], microwave emission[71-74], and flame-photometric[69] detectors. An atomic-absorption spectrometer with flameless atomisation can be used for the detection of volatile compounds of metals[75]. The Table lists data on the use of metal chelates in quantitative gas-chromatographic analysis.

VI. BEHAVIOUR OF METAL CHELATES IN A CHROMATOGRAPHIC COLUMN

Volatile complexes of metals are extremely capricious in chromatographic behaviour. Hitherto no objective methods have been available for assessing the suitability of a particular chelate for quantitative gas-chromatographic analysis. The widely used thermogravimetric

analysis permits merely comparison of the relative volatilities of two or more chelates and may indicate whether a given chelate will sublime without decomposition. Quite often a chelate that appears to be "ideal" from thermogravimetric data proves to be unsatisfactory for gas chromatography.

Especially marked departures from "ideality" are observed in work with small quantities of the substance. The literature is full of descriptions of such phenomena as irreversible sorption of the initial portions of chelates in columns[30], distortion of the form of the peak and diminution in the efficiency of the column as the sample becomes smaller[21], redox reactions in the column[20], non-linearity of the calibration curve on dilution of the test solutions (the curve does not pass through the origin)[30,34,38,73], sorption of the chelate by the surface of the liquid phase[30,76], displacement of one sorbed chelate by another[30], anomalous broadening of the chelate peaks with lengthening of the column[29], etc. The anomalous behaviour of chelates in columns has been explained[77] by their dissociation in the liquid phase, a hypothesis apparently supported by the fact that addition of a small quantity of the vapour of the ligand to the carrier gas improves the chromatograms of certain chelates[73,77,78]. Incidentally, surprisingly little attention had been paid until recently to the role of the liquid phase in the chromatography of chelates, although even the unusual fact that metal chelates can in the large majority of cases be satisfactorily chromatographed only on polysiloxane liquid phases and Apiezon L should have interested research workers. Indeed, recent results show that polysiloxanes and Apiezon L are by no means the best liquid phases for the gas chromatography of chelates. Thus the chromatograms of several chelates are considerably improved by use of the liquid phase Dexsil-300 GH based on carboranes[30,47].

Other facts difficult to explain may be mentioned. For example, it is difficult to understand the sharp differences in the sensitivity of a flame-ionisation detector to chelates of rare-earth metals having closely similar properties. Thus the sensitivity of detection of mixed-ligand complexes of erbium and ytterbium with decafluoroheptanedione and dibutyl sulphoxide differs by a factor of 8,[29] whereas that of chelates of neodymium and samarium by a factor of ~ 11![28] Another little understood phenomenon[26] is that the chelate peak gradually diminished on successive admissions to the column of the terbium complex of dipivaloylmethane, and the chromatogram became stable only after several additions of a benzene solution of the dione. The problem of the behaviour of metal chelates in a chromatographic column obviously requires further investigation.

REFERENCES

1. B.I. Anvaer and Yu.S. Drugov, Zhur. Anal. Khim., 26, 1180 (1971).
2. D.N. Sokolov, Zhur. Anal. Khim., 27, 993 (1972).
3. L. Gasco and T.H. Risby, Energ. nucl. (Esp.), 16, 421 (1972).
4. R. Belcher, Pure Appl. Chem., 34, 13 (1973).
5. P. Jacquelot and G. Thomas, Bull. Soc. chim. France, 1261 (1973).
6. J.A. Rodriguez-Vazquez, Analyt. Chim. Acta, 73, 1 (1974).
7. A.A. Zhukhovitskii, V.G. Guglya, D.N. Sokolov, and B.I. Anvaer, Zhur. Vses. Khim. Obshch. Mendeleeva, 16, 565 (1971).
8. C. Pommier and G. Guiochon, "La Chromatographie en Phase gazeuse en Chimie inorganique", Paris, 1971.
9. Okubo Teiji and Aoki Fumio, J. Chem. Soc. Japan, Chem. and Ind. Chem., 1681 (1973).
10. Okubo Teiji and Aoki Fumio, J. Nat. Chem. Lab. Ind., 69, 44 (1974).
11. Kuwamoto Tooru, Japan Analyst, 21, 445 (1972).
12. P. Jacquelot and G. Thomas, J. Chromatog., 66, 121 (1972).
13. Tanikawa Keiti, Oti Hisao, and Arukawa Keiti, Japan Analyst, 19, 1669 (1970).
14. Utsunomiya Kei, Bull. Chem. Soc. Japan, 44, 2688 (1971).
15. Kito Akira, Miyake Yoshizo, Kobayashi Hiroshi, and Ueno Keihei, Japan Analyst, 20, 1363 (1971).
16. P. Jacquelot and G. Thomas, Bull. Soc. chim. France, 702 (1971).
17. Shigematsu Tsunenobu, Tsutomu Uchiike, Toru Aoki, and Masakazu Matsui, Bull. Inst. Chem. Res., Kyoto Univ., 51, 273 (1973).
18. R.F. Sieck, J.J. Richard, K. Iversen, and C.V. Banks, Analyt. Chem., 43, 913 (1971).
19. P. Jacquelot, J.P. Meille, and G. Thomas, Analyt. Chim. Acta, 60, 335 (1972).
20. B.B. Tomažic and J.W. O'Laughlin, Analyt. Chem., 45, 1519 (1973).
21. C.A. Burgett, J. Chromatog. Sci., 11, 611 (1973).
22. R. Belcher, J. Majer, R. Perry, and W.I. Stephen, J. Inorg. Nuclear Chem., 31, 471 (1969).
23. M.Z. Gurevich, T.M. Sas, B.D. Stepin, and V.V. Zelentsov, Zhur. Neorg. Khim., 16, 1748 (1971) [Russ. J. Inorg. Chem., No. 6 (1971)].
24. K.J. Eisentraut and R.E. Sievers, J. Amer. Chem. Soc., 87, 5254 (1965).
25. Kito Akira and Miyake Yashizo, Bull. Govt. Ind. Res. Inst. Osaka, 25, 93 (1974).
26. Kei Utsunomiya, Analyt. Chim. Acta, 59, 147 (1972).
27. Kei Utsunomiya and Shigematsu Tsunenobu, Bull. Chem. Soc. Japan, 45, 303 (1972).
28. C.A. Burgett and J.S. Fritz, Talanta, 20, 363 (1973).
29. C.A. Burgett and J.S. Fritz, Analyt. Chem., 44, 1738 (1972).
30. C.A. Burgett and J.S. Fritz, J. Chromatog., 77, 265 (1973).
31. R.F. Sieck and C.V. Banks, Analyt. Chem., 44, 2307 (1972).
32. Shigematsu Tsunenobu, Matsui Masakazu, and Utsunomiya Kei, Bull. Chem. Soc. Japan, 42, 1278 (1969).
33. W.I. Stephen, I.J. Thomson, and P.C. Uden, Chem. Comm., 269 (1969).
34. R. Belcher, W.I. Stephen, I.J. Thomson, and P.C. Uden, J. Inorg. Nuclear Chem., 33, 1851 (1971).
35. R. Belcher, W.I. Stephen, I.J. Thomson, and P.C. Uden, J. Inorg. Nuclear Chem., 34, 1017 (1972).
36. R. Belcher, W.I. Stephen, I.J. Thomson, and P.C. Uden, Chem. Comm., 1019 (1970).
37. R. Belcher, W.I. Stephen, I.J. Thomson, and P.C. Uden, J. Inorg. Nuclear Chem., 33, 1851 (1971).
38. R.S. Barratt, R. Belcher, W.I. Stephen, and P.C. Uden, Analyt. Chim. Acta, 59, 59 (1972).
39. E. Bayer and H.P. Müller, Tetrahedron Lett., 533 (1971).
40. E. Bayer, H.P. Müller, and R.S. Sievers, Analyt. Chem., 43, 2012 (1971).
41. M. Mijazaki, T. Imanari, T. Kunugi, and Z. Tamura, Chem. and Pharm. Bull. (Japan), 14, 117 (1967).

42. R. Belcher, M. Pravica, W. I. Stephen, and P. C. Uden, Chem. Comm., 41 (1971).
43. R. Belcher, R. J. Martin, W. I. Stephen, D. E. Henderson, A. Kamalizad, and P. C. Uden, Analyt. Chem., 45, 1197 (1973).
44. P. C. Uden and K. Blessel, Inorg. Chem., 12, 352 (1973).
45. R. Belcher, K. Blessel, T. Cardwell, M. Pravica, W. I. Stephen, and P. C. Uden, J. Inorg. Nuclear Chem., 35, 1127 (1973).
46. P. C. Uden, D. E. Henderson, and A. Kamalizad, J. Chromatog. Sci., 12, 591 (1971).
47. P. C. Uden and D. E. Henderson, J. Chromatog., 99, 309 (1974).
48. G. D'Ascenzo and W. W. Wendlandt, J. Therm. Anal., 1, 423 (1969).
49. B. Flaherty and G. McCutcheon, J. Therm. Anal., 3, 75 (1971).
50. R. S. Barratt, R. Belcher, W. I. Stephen, and P. C. Uden, Analyt. Chim. Acta, 57, 447 (1971).
51. A. Kleinmann and R. Neeb, Naturwiss., 60, 201 (1973).
52. W. C. Butts and W. T. Rainey, Analyt. Chem., 43, 538 (1971).
53. R. Bock and A. Monerjan, Z. analyt. Chem., 235, 317 (1968).
54. G. Schwedt and H. A. Rüssel, Chromatographia, 5, 242 (1972).
55. G. Schwedt and H. A. Rüssel, Z. analyt. Chem., 264, 301 (1973).
56. Yu. S. Drugov, G. V. Murav'eva, K. M. Grinberg, G. N. Nesterenko, and D. N. Sokolov, Zavod. Lab., 38, 1305 (1972).
57. K. J. Eisentrant, D. J. Griest, and R. E. Sievers, Analyt. Chem., 43, 2003 (1971).
58. M. S. Black and R. E. Sievers, Analyt. Chem., 45, 1773 (1973).
59. G. Kaiser, E. Grallath, P. Tschöpel, and G. Tölg, Z. analyt. Chem., 259, 257 (1972).
60. M. L. Taylor and E. L. Arnold, Analyt. Chem., 43, 1328 (1971).
61. C. Genty, C. Houin, P. Malherbe, and R. Schott, Analyt. Chem., 43, 235 (1971).
62. Lee Meng-Lein and D. C. Burrell, Analyt. Chim. Acta, 66, 245 (1973).
63. D. N. Sokolov, G. N. Nesterenko, and L. K. Golubeva, Zavod. Lab., 39, 939 (1973).
64. W. D. Ross, W. G. Scribner, and R. E. Sievers, "Gas Chromatography 1970", London, 1971, p. 369.
65. Yeh Si-Jung and Ke Chin-Nan, J. Chinese Chem. Soc., 20, 129 (1973).
66. J. Savory, P. Mushak, F. W. Sunderman, P. H. Estes, and N. O. Roszel, Analyt. Chem., 42, 294 (1970).
67. L. C. Hansen, W. G. Scribner, T. W. Gilbert, and R. E. Sievers, Analyt. Chem., 43, 349 (1971).
68. G. H. Booth and W. J. Darby, Analyt. Chem., 43, 831 (1971).
69. R. Ross and T. Shafik, J. Chromatog. Sci., 11, 46 (1973).
70. W. R. Wolf, M. L. Taylor, B. M. Hughes, T. O. Tiernan, and R. E. Sievers, Analyt. Chem., 44, 616 (1972).
71. R. M. Dagnall, T. S. West, and P. Whitehead, Analyst, 98, 647 (1973).
72. F. A. Serravallo and T. H. Risby, J. Chromatog. Sci., 12, 585 (1974).
73. Kawaguchi Hiroshi, Sakamoto Takeshi, Yoshida Yuji, and Mizuike Atsuchi, Japan Analyst, 22, 1434 (1973).
74. Kawaguchi Hiroshi, Sakamoto Takeshi, and Mizuike Atsuchi, Talanta, 20, 321 (1973).
75. D. A. Segar, Analyt. Lett., 7, 89 (1974).
76. R. Fontaine, C. Pommier, C. Eon, and G. Guiochon, J. Chromatog., 104, 1 (1975).
77. Fujinaga Taitiro, Kuwamoto Tooru, and Murai Shigeo, Talanta, 18, 429 (1971).
78. Taitiro Fujinaga, Tooru Kuwamoto, and S. Murai, Analyt. Chim. Acta, 71, 141 (1974).

Chernogolovka Branch,
Institute of Chemical Physics,
USSR Academy of Sciences