Translated from *Uspekhi Khimii*, **57**, 1670-1687 (1988) U.D.C. 543.544.541.49

Analytical Gas Chromatography of Volatile Metal Complexes

D.N.Sokolov

The recent advances in the gas chromatography of volatile metal complexes such as β-diketonates, adducts of β-diketonates with neutral donors, dialkyldithiocarbamates, β-ketoaminates, and other compounds are examined. Attention is mainly focused on methods for determining trace metals, capillary chromatography, chromatography in ligand vapour, and studies on the abnormal behaviour of metal chelates on a chromatography column.
The bibliography includes 138 references.

CONTENTS

I.	Introduction	956
II.	Metal β-diketonates	956
III.	Adducts of β-diketonates with neutral donors	958
IV.	Complexes of metals with nitrogen- and sulphur-containing ligands	958
V.	Gas chromatographic separation of metal chelates on capillary columns	961
VI.	Gas chromatography of metal β-diketonates in ligand vapour	963
VII.	Behaviour of metal chelates on a chromatography column	963
VIII.	Gas chromatographic determination of trace metals	964

I. INTRODUCTION

The present review covers the period from the middle of 1975 to the end of 1986. During these 11 years there was a marked development of research into the gas chromatography of volatile metal complexes. About 120 original articles, a number of reviews,[1-17] and two monographs[18,19] which are completely or partly devoted to this topic have been published. Since in the preceding five-year period (1970–1975), which was covered in a previous review,[5] about 70 articles, including 7 reviews, were published, it is evident that the growth rate of research in this field has remained approximately the same. The main trends have also not changed significantly; these are either a comparative study of the properties of new volatile metal compounds that are united by some common feature (mostly these are complexes of a number of metals with one or more ligands or complexes of a single metal with a number of ligands) or better separation and improved sensitivity for determining those complexes already known.

Research into new volatile metal compounds has been conducted with considerable vigour. In addition to the traditional β-diketonates and β-ketoaminates, a large number of adducts of metal β-diketonates with neutral donors have been synthesised and studied as also have dialkyldithiocarbamates, dialkylthiophosphates, and analogues of β-diketonates that contain donor atoms of oxygen, sulphur, and nitrogen in different combinations. Several studies on the gas chromatography of metalloporphyrins have appeared.

As regards chromatographic experimental technique, mention can be made of the further development of gas chromatography using carrier gas into which the vapour of a ligand is introduced (GCLV) as well as the appearance of a promising new field—chromatography of metal chelates on glass and quartz capillary columns.

As before the most popular detectors are the flame ionisation detector and electron capture detector, although in some studies new ones such as microwave plasma, nitrogen-phosphorus, and flame photometric detectors are used. The heat-transfer detector is now rarely used. The use of chromatography–mass spectrometry has become quite common.

A considerable section of research is devoted to the practical application of gas chromatography in determining small traces of metals in a particular substance. Mention can be made here of the increase in the number of determinable metals and the improvement in sensitivity for determining many of them.

II. METAL β-DIKETONATES

β-Diketonates were the first volatile metal complexes to be used in gas chromatography. During the last two decades they have been thoroughly studied. However, even at the present time this class of compounds continues to attract the attention of research workers. Volatile β-diketonates of about forty metals have been synthesised. The most suitable for gas chromatography are metal complexes with β-diketones that contain *tert*-butyl and perfluoroalkyl substituents. The attraction in using β-diketonates for analysis lies in the fact that in most cases the ion being determined can readily and rapidly be converted quantitatively into a volatile chelate by extracting it from aqueous solution with a solution of the appropriate β-diketone in a non-polar organic solvent. However, the β-diketonates of many metals are kinetically labile and have insufficient thermal stability, which leads to their partial decomposition and irreversible adsorption on the chromatography column. As a result, abnormal effects occur during separation which prevent the widespread use of β-diketonates in quantitative analysis.[18]

Therefore, only the most stable β-diketonates of chromium(III), aluminium(III), beryllium(II), cobalt(III), and a few others are of practical use.

Numerous attempts using different methods to expand this list have not produced tangible results. An exception to this is the gas chromatography in ligand vapour (GCLV) proposed by Japanese authors, which will be examined below. However, this method is technically complex and excludes the use of the most common detectors (flame ionisation and electron capture), which considerably reduces its practical value.

1. Non-fluorinated β-Diketonates

Only a few studies in recent years have been devoted to non-fluorinated β-diketonates. The chromatographic behaviour of chromium and beryllium acetylacetonates and chromium propionylacetonates on different liquid phases has been investigated and it has been shown that beryllium acetylacetonate decomposes to a considerable extent on chromatography columns.[20] The satisfactory separation of chromium, aluminium, and cobalt(III) acetylacetonates on a column (1 m × 4 mm) with 5% Silicone OV-17 on Chromosorb W using a programmed increase in temperature from 190 to 250 °C (8 K/min) has been reported.[21,22] The gas chromatographic determination of aluminium as its acetylacetonate in soils has been reported[23] and a method has been developed[24] for determining copper in catalysts (also in the form of its acetylacetonate). The quantitative analysis of certain rare earth elements in the form of dipivaloylmethanates has been carried out.[25] One study,[26] in which for the first time gas chromatographic separation of rare earth acetylacetonates was achieved, is of interest. However, the gas chromatographic properties of these complexes are far from perfect and the separation of chelates of adjacent rare earth elements was not achieved. It was found that rare earth β-diketonates can react with vaporised β-diketonates, including acetylacetone (AA), in both the gas and condensed phases to give mixed ligand complexes.[27]

The use of non-fluorinated metal β-diketonates in gas chromatography is not likely to be of future interest. Only dipivaloylmethanes, which are of interest for the separation of rare earths and other metals, constitute an exception to this.

2. Fluorinated β-Diketonates

A considerably larger number of articles have been devoted to the volatile metal chelates with fluorine-containing β-diketonates. The chromatographic behaviour of vanadium(III) and vanadyl chelates with trifluoroacetylacetone (TFA), pivaloyltrifluoroacetone (PTA), and heptafluorodimethyloctanedione (HDO) has been studied.[28,29] It was shown that the chromatographic properties of vanadyl chelates were unsatisfactory. In addition to the usual abnormal effects (adsorption of the first samples of chelate on the column and a non-linear calibration curve at low concentrations), a partial reduction of vanadium(IV) to vanadium(III) also occurred on the column.

Vanadium(III) β-diketonates have better chromatographic properties. Particularly good results were obtained when studying a vanadium(III) chelate with HDO, which displayed virtually no abnormal effects. Volatile chelates of molybdenum(V) and (IV) with β-diketones that contain terminal CF_3, C_3F_7 or $C(CH_3)_3$, CH_3, thienyl, furyl, C_6H_5, and camphorate groups have been synthesised.[30] The authors claim that these chelates can be used in gas chromatography and also for improving the sensitivity of the atomic absorption method for analysing molybdenum. The thermal stability and chromatographic behaviour of chelates of copper and erbium with ten β-diketones that contain terminal CF_3, $C(CH_3)_3$, C_6H_5, and CH_3 groups have groups have been studied. As was to be expected almost all the copper complexes proved to be suitable for gas chromatography but the thermal stability of the erbium chelates was in most cases insufficiently high.

The chromatographic behaviour of complexes of aluminium, vanadium(III), chromium(III), iron(III), manganese(III), cobalt(III), and copper(II) with β-diketones containing terminal CF_3, C_2F_5, C_3F_7, CH_3, $CH(CH_3)_2$, and $C(CH_3)_3$ groups has been studied[32] on glass columns with Silicone SE-30 deposited on different solid supports.

Chelates of thallium(I) with PTA and HDO and thallium(III) with TFA, PTA, and HDO have been synthesised.[33] All these chelates can be satisfactorily chromatographed in microgram quantities on a glass column (75 × 0.4 cm) with 5% Silicone DC-550 on Chromatotone N AW DCMS at 170 °C, and thallium(I) compounds are retained to a considerably greater extent than thallium(III) compounds. Partial decomposition of the compounds studied on the column was recorded.

In a number of studies into the behaviour of volatile β-diketonates, compounds labelled with radioisotopes have been used. Thus, Buchtela et al.[34] chromatographed aluminium and chromium acetylacetonates and a number of rare earth complexes with HDO using ligands labelled with tritium. A flame ionisation detector and proportional counter were used for detection, and in the latter case it was possible to record a low detection limit for chromium ($\sim 10^{-15}$ g).

The gas chromatographic determination of chromium labelled with ^{51}Cr as a complex with hexafluoroacetylacetone (HFA) has been reported.[35] A gas-flow counter was used for detection. High accuracy in determining the isotope ratios for a number of alkaline-earth and transition metals (magnesium, calcium, chromium, iron, nickel, copper, cadmium, zinc) was achieved with the use of gas chromatography–mass spectrometry.[36] The metals were converted to complexes with TFA, PTA, or HDO or to diethyldithiocarbamates (DEDTC); separation was effected on a glass column with 1% or 6% Silicone SE-30 on Gas-Chrom Q. The authors maintain that the method is suitable for determining alkaline-earth and transition metals in natural materials using a mass spectrometric version of isotopic dilution.

The separation of geometric isomers of molybdenum(III) trifluoroacetylacetonates has been carried out.[37] The isolated preparatively pure complexes were identified from their electronic spectra, solubility, and melting points.

In one study[38] the suitability of a nitrogen-phosphorus detector for chelates with AA, TFA, and HFA was investigated. The sensitivity of the nitrogen-phosphorus detector proved to be comparable to that of the electron capture detector.

Volatile chelates of zirconium(IV) and hafnium(IV) with AA, TFA, and HFA have been synthesised, and their thermal stability and suitability for gas chromatography investigated.[39] Mikhailenko and Sereda[40] synthesised chromium(III) chelates with fifteen different β-diketones, carried out thermogravimetric analysis of these compounds, determined their dipole moments, and found that there was no correlation between the magnitude of the dipole moments and the retention times of the chelates studied. A number of thermodynamic values specific to the gas–liquid equilibrium for several stationary phases were also determined.

Several studies are devoted to the application of gas chromatography of β-diketonates for the practical analysis of metals in various substances. There have been reports on the determination of beryllium as a complex with TFA in natural and waste water[41] and also in tap water and uranium oxide[42] and in metal alloys.[43] The determination of aluminium and chromium (also as chelates with TFA) in aqueous solution at concentrations down to $10^{-6}-10^{-7}$ g/litre has been reported,[44] and the determination of vanadium in polymers, complex compounds, and petroleum has been described.[45,46] The determination of small quantities of chromium in various substances has also been the subject of studies.[47-51]

A method for determining traces of ruthenium in car exhaust gases in the form of a trifluoroacetylacetonate has been developed.[52] The detection limit for ruthenium reached 2.4×10^{-13} g. A method for determining aluminium and copper as complexes with PTA in glasses and alloys has been reported.[53]

III. ADDUCTS OF β-DIKETONATES WITH NEUTRAL DONORS

In recent years research workers have shown increased interest in adducts of metal β-diketonates with neutral donors. This applies particularly to complexes with HFA. As was indicated,[18] metal chelates with HFA were not of particular interest for a long time because of the tendency of HFA to react with water to give tetrahydroxy compounds incapable of forming complexes with metals. It transpired, however, that in the presence of neutral donors such as dibutyl sulphoxide (DBSO), tributyl phosphate (TBP), etc., adducts can be synthesised (usually containing one or two donor molecules) by normal extraction from aqueous solutions.[54,56,57]

In this connection a number of studies on the gas chromatography of compounds of this class have recently appeared. Thus, the gas chromatographic behaviour of adducts of manganese(II), iron(II), cobalt(II), and nickel(II) hexafluoroacetylacetonates with TBP and DBSO has been investigated.[54] Preliminary experiments showed that when TBP was used as a neutral donor the chromatographic peak from the donor was superimposed on the adduct peaks, so the studies were mainly conducted on adducts with DBSO. The metal ions were extracted from aqueous solutions at pH 5.0–5.5 with a solution of a mixture of HFA and DBSO in cyclohexane. All the adducts obtained by this method had the composition ML_2. .2DBSO (where M is metal ion, L is HFA anion). Separation was carried out on a glass column (25. × 0.3 cm) with 5% Dexsil-300 on Chromosorb W HP. The packing was silanised directly in the column. It was found that the concentration of DBSO in solution had little effect on the stability of the adducts. For all the adducts adsorption effects of the first samples of complex in the column, which are common for simple β-diketonates, and a column "memory" effect occurred. The presence of the respective metals in the adducts was confirmed by atomic absorption spectroscopy.

The behaviour of adducts of manganese(II), iron(II), cobalt(II), and copper(II) β-diketonates with neutral donors such as dimethylformamide (DMF) and tributylphosphine oxide (TBPO) has been studied.[55] A study of the thermal properties of anhydrous and hydrated manganese(II) β-diketonates and adducts of manganese(II) hexafluoroacetylacetonate with DMF and TBPO showed that introduction of a neutral donor into the molecule of complex considerably increased the thermal stability of the molecule and made it possible to sublime the complex almost without decomposition at 100–130 °C. Satisfactory chromatograms were obtained for adducts of hexafluoroacetylacetonates of the metals listed above for DMF and TBPO on a glass column (125 × 0.4 cm) with 5% Silicone SE-30 at 100 °C and their retention times were determined.

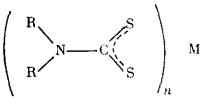
A radioactive indicator method was used to study the extraction of scandium, chromium(III), manganese(II), iron(III), cobalt(II), copper, zinc, yttrium, silver, cadmium, lanthanum, cerium(II). europium(III), ytterbium(III), mercury(II), thorium(IV), uranium(IV) and (VI), vanadium(IV), and americium(III) ions from aqueous solutions at pH 3.0–3.3 with cyclohexane solutions containing stoichiometric quantities of HFA and neutral donors such as *n*-butylamine, isobutylamine, *tert*-butylamine, TBP, TBPO, and trioctylphosphine oxide (TOPO).[56] The adducts obtained were studied thermogravimetrically. It transpired that the adducts with TBPO had the highest volatility. The chromatographic behaviour of these adducts was studied on different packings with programmed temperature change in the range 180–250 °C. The elution temperatures were found for a number of adducts of metal hexafluoroacetylacetonates with TBPO.

In a later study the same authors[57] studied adducts of rare earth hexafluoroacetylacetonates with TOPO, TBPO, TBP, tetrahydrofuran, *n*-butylamine, and dodecylamine. In this case adducts with TBPO also had the best properties as regards gas chromatography. Chromatographic separation was carried out on glass columns (60 × 0.4 cm or 90 × 0.4 cm) with 10% Silicone OV-101 or Dexsil-300 on Chromosorb W HP. The temperature was raised from 180 to 250 °C at a rate of 2 K/min, and a flame ionisation detector was used. Out of all the rare earth adducts the peaks from samarium, terbium, dysprosium, holmium, erbium complexes were effectively resolved on the chromatogram, the remaining peaks were only partially resolved.

IV. METAL COMPLEXES WITH NITROGEN- AND SULPHUR-CONTAINING LIGANDS

1. Dialkyldithiocarbamates

Recently chromatography researchers have shown increased interest in dialkyldithiocarbamates (DADTC) of metals with the general formula:



where M is a metal ion and *n* is its charge. The first report on the chromatographic separation of copper, nickel, and zinc DADTC appeared in 1969,[58] but a systematic study of the suitability of compounds of this class for gas chromatography has only started since 1975. Not long afterwards di(trifluoroethyl)dithiocarbamates (DTFEDTC), which have a higher volatility and better chromatographic properties, were synthesised.[59]

Non-fluorinated DADTC are less volatile than β-diketonates and are usually chromatographed at higher temperatures (in the region of 170–230 °C). Although there are not infrequent indications in the

literature that metal DADTC complexes partially decompose on columns or during thermogravimetric studies, there are virtually no reports about the type of abnormal effects that occur when using β-diketonates, such as adsorption of the first samples of chelate on a new column or the column "memory" effect. This is probably due to the greater kinetic stability of dialkyldithiocarbamates, which inhibits the rapid exchange of ligands between complexes. Satisfactory chromatographic properties are mainly displayed by DADTC chelates of bivalent ions (copper, nickel, zinc, and others), but some authors also managed to chromatograph complexes of chromium(III), iron(III), gold(III), thallium(I), antimony(III), bismuth(III), indium(III), and rhodium(III).[62,67-69,73,105,107]

DADTC complexes are even more convenient than β-diketonates as regards their practical application. A quantitative conversion of the ions being determined to the corresponding complexes is carried out by extracting them from aqueous solution as in the case of β-diketonates. But while the chromatographic determination of small quantities of metals as β-diketonates is only possible using expensive β-diketones with perfluoroalkyl substituents, in the case of DADTC perfectly satisfactory results are often obtained using readily available diethyldithiocarbamates (DEDTC).

In one study[60] the chromatographic behaviour of seven different nickel(II) DADTC that contained CH_3, C_2H_5, C_3H_7, H, *iso*-C_4H_9, and C_5H_{12} groups as terminal substituents was examined. The best results were obtained with diethyl derivatives. In the chromatogram of a mixture of diethyl, di-*n*-propyl, and di-*n*-butyl complexes of nickel shown in this study[60] there were no peaks from chelates with mixed ligands, which is confirmation of the kinetic stability of dialkyldithiocarbamate complexes.

The separation of nickel, copper, and zinc diethyldithiocarbamates on a glass column (60 × 0.3 cm) with 3% Silicone OV-25 at 260 °C has been reported.[61] The same authors[62] carried out the separation of lead(II), nickel, copper, cadmium, and zinc DEDTC under approximately the same conditions as well as di(trifluoroethyl)-dithiocarbamates (DTFEDTC) of nickel, copper, and zinc (in the same mixture) and bismuth(III), antimony(III), lead(II), cadmium, nickel, and zinc (in another mixture) at temperatures of 240 °C and 185 °C respectively on a column with 5% Silicone SE-30 on Chromosorb W. It was possible to determine a number of metal cations down to concentrations of 6×10^{-5}% using a flame ionisation detector.

The possibility of detecting small quantities of zinc, cadmium, nickel, mercury(II), and lead(II) DEDTC using an electron capture detector with ^{63}NI was examined, and it was found that the detection limit for lead complexes was 6 ng and 2–4 ng for the remaining complexes in a sample.[63] In some cases the peaks from the pure zinc and cadmium chelates were split. The explanation for this given by the authors is that the respective complexes are present in the system in both the monomer and dimer forms. However, this phenomenon was only observed in this study. The determination of zinc, copper, and nickel as their DEDTC complexes in marine residues and in other substances has been reported.[64,65]

In one study[66] the chromatographic behaviour was examined and mass spectra obtained for copper, cadmium, cobalt, zinc, and nickel DEDTC and partial decomposition of the copper, cobalt, and cadmium complexes was detected on a column with Silicone SE-30 using different solid supports. For the quantitative determination of nickel and zinc DADTC the use of a column with 2% Silicone SE-30 on Chromosorb G AW DMCS or on Gas-Chrom Q was recommended. For the first time the separation of a number of DADTC complexes was also carried out on a glass capillary column of length 31.4 m with Silicone OV-101. Mass spectrometric analysis showed that with an increase in length of alkyl substituents in a DADTC molecule the degree of decomposition of the chelate on evaporation increased.

A method for determining chromium(III) and chromium(VI) in aqueous solution by their combined presence as DTFEDTC complexes has been developed.[67] The best results were obtained on packed columns with 3% Silicone OV-25 at 160–210 °C or Silicone OV-101 at 190–230 °C. The minimum concentration of chromium that could be detected was 5×10^{-5}%. Cobalt(II), nickel, zinc, cadmium, lead(II), copper, and iron(III) ions inferred with the determination. Similar methods have been reported in other studies.[68,69]

Meyer and Neeb[70] chromatographed nickel and cobalt DTFEDTC on packed columns with Silicone OV-101 (3%) deposited on different supports. When Chromosorb W HP was used on a glass column (90 × 0.25 cm) with programmed temperature change (2 K/min) in the range 135–200 °C, using a flame ionisation detector it was possible to detect down to 1×10^{-6}% nickel and cobalt in solution in the presence of tenfold quantities of copper, cadmium, and zinc and thousandfold quantities of iron.

The determination of rhenium(IV), (V), and (VII) in aqueous solution as DADTC complexes with ethyl and phenyl terminal groups has been reported.[71] The complexes were extracted with chloroform from hydrochloric acid solutions. Separation was carried out on a glass column of length 0.6 m with 5% Silicone SE-30 on Chromatone N AW DMCS.

A comparison of the suitability of different solid supports for the quantitative gas chromatographic determination of nickel and zinc DEDTC [72] showed that Chromosorb W HP and Chromatone N-Super had the best properties and that Chromosorb G was the least suitable.

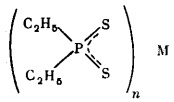
One study[73] is concerned with the determination of noble metal ions [gold(III), platinum(IV), palladium(II), rhodium(III), and iridium(IV)] as complexes with DTFEDTC. It should be noted that this is the first report on the quantitative gas chromatographic determination of gold. Separation was carried out on a glass column (80–100 × 0.2 cm) with 3% Silicone OV-3 on Chromosorb G AW DMCS at 210–220 °C using an electron capture detector with ^{63}Ni. The sensitivity for determination was comparable to the sensitivity of atomic absorption spectroscopy with electrothermal atomisation and in a number of cases even exceeded the latter.

In a study of the chromatographic behaviour of copper and nickel complexes with fifteen different DADTC on OV-101, NGA, and OV-225 liquid phases it was found that the shortest retention times were typical for chelates with short alkyl terminal groups if chromatography was carried out on a polar liquid phase.[74]

One study[75] is concerned with developing a method for determining trace metals as DEDTC complexes in aqueous solution. Analysis of small quantities of nickel, copper, zinc, cadmium, mercury, lead, and cobalt on columns of length 30–60 cm containing mixures of siloxane liquid phases—SE-30, QF-1, OV-101—on Gas-Chrom Q and Chromosorb W HP showed that lead, cadmium, and mercury DEDTC displayed signs of decomposition during the experiment. When a flame ionisation detector was used the limiting dilutions for the different metals ranged from 17 to 300 ng/ml. It is interesting to note that the authors carried out the experiments not only on glass columns but also on metal columns and found that in the latter case the detection limits increased by a factor of about one and a half.

2. Dialkyldithiophosphinates and Dialkyldithiophosphates

Kleinman and Neeb[76] synthesised diethyldithiophosphinates (DEDTP) of zinc, cadmium, cobalt, nickel, and lead with the general formula

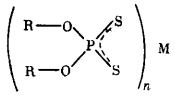


Thermogravimetric studies showed that all of the compounds obtained partially decomposed on sublimation (the non-volatile residue amounted to 2–11%). Nevertheless, the authors[76] prepared chromatograms of several mixtures of these compounds, including mixtures of zinc, cadmium, nickel, and lead DEDTP. Separation was carried out on a glass column (78 × 0.3 cm) with 3% Silicone OV-17 on Chromosorb N AW. Less satisfactory results were obtained when SE-30, OV-101, and Apiezon L were used as liquid phases. The cobalt complex was apparently not suitable for gas chromatography.

Somewhat later[77] the chromatographic behaviour of DEDTP complexes of the same metals was studied on columns with different silicone liquid phases on Chromosorb Q. The authors maintained that the lead chelate rapidly decomposed in solution on exposure to light. A method for determining traces of cadmium in aqueous solution at concentrations down to 3×10^{-6}% in the presence of a hundredfold excess of zinc is reported in the study.

The gas chromatographic behaviour of nickel, zinc, and cadmium di-isopropyldithiophosphinates under much the same conditions has also been reported[78] and the partial decomposition of the cadmium complexes was recorded. It was possible to detect these chelates in solution when their concentration was $\sim 2 \times 10^{-6}$ moles/litre.

Two studies[79,80] are devoted to the gas chromatography of

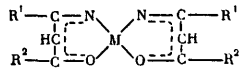


volatile dialkyldithiophosphates. From among the dimethyl- and diethyl-dithiophosphate complexes of nickel, palladium, and platinum, the di-*n*-propyldithiophosphate complexes of nickel and palladium, and the di-isopropyldithiophosphate chelates of zinc, nickel, palladium, platinum, copper, mercury(II), chromium(III), rhodium(III), cobalt(III), gold(III), ruthenium(III), and iridium(III) that were synthesised only the dimethyl- and di-isopropyl-dithiophosphates of nickel, palladium, platinum, chromium(III), and rhodium(III) proved to be suitable for gas chromatography.[79] The best chromatograms were obtained on columns with Silicone OV-101, SE-30, and PS-300 on Gas-Chrom Q or Chromosorb 750 at 150–180 °C.

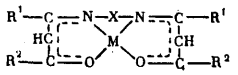
The later study[80] described the chromatographic behaviour of diethyldithiophosphates of a number of metals on packed and capillary columns. When a flame ionisation detector was used the detection limits reached 10^{-11}–10^{-12} g of metal.

3. β-Ketoaminates and Metal Complexes with Ligands Containing S, O and S, N Donor Pairs

Bidentate and tetradentate β-ketoaminates (sometimes also called β-aminovinylketones, β-ketoimines, and Schiff bases) are formed by condensation of β-diketones with mono- or di-amines. They form chelate complexes with many metal ions. It is mainly β-ketoamine complexes with bivalent copper ions and metal ions of the nickel group that are suitable for gas chromatography:[18]



bidentate β-ketoamine complex



tetradentate β-ketoamine complex (X—hydrocarbon chain)

When considering bidentate β-ketoamines as ligands there is practical interest mainly in ketoamines obtained by condensation of diketones with ammonia, since metal complexes with N-alkyl-substituted β-ketoamines are thermally unstable and tend to hydrolyse. Unfortunately, even the most stable metal chelates with bidentate β-ketoamines fairly readily eliminate ligands on heating. As a result of this they usually decompose on the column during chromatography, which gives rise to abnormal effects.[18]

Complexes with tetradentate β-ketoamines are in most cases more stable and have better chromatographic properties despite their lower volatility. Under optimum conditions using an electron capture detector, such chelates can be detected using chromatography down to 10^{-12} g. Fluorinated complexes have particularly good properties. However, their practical application in analysis is made difficult by the extremely low solubility of fluorinated tetradentate β-ketoamines in water, which inhibits the use of the usual extraction methods for quantitative conversion of a metal being determined into the respective complex. The problems in the analytical use of β-ketoaminates have been examined in detail in a monograph.[18]

Attempts to use salicylaldiminate complexes of copper, nickel, and zinc for gas chromatography did not give favourable results.[18,81]

The thermal stability and chromatographic behaviour of 2-picolylalkylketonates [82] and 2-picolyltrifluoromethylketones [83] of beryllium, copper, zinc, nickel, and chromium were studied. It was found that the chelates of all the metals investigated apart from chromium were suitable for quantitative gas chromatographic analysis. However, the detection limits of these complexes were not stated.

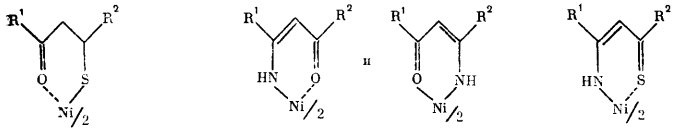
The volatility and chromatographic behaviour of vanadyl,[84–87] copper, nickel,[84,86,87] and iron(III) [88] complexes with certain Schiff bases were studied. Satisfactory results were obtained when 1,1,1,1′,1′,1′-hexafluoro-4,4′-(1-methylethane-1,2-diyldi-imino)*bis*-(pent-3-en-2-one) [86] and 2,2,2′,2′-tetramethyl,5,′-(ethane-1,2-diyldi-imino)*bis*(hex-4-en-3-one) [85] were used as ligands for the determination of nanogram quantities of copper, nickel, and vanadium in petroleum and biological materials.

The simultaneous determination of copper and nickel as complexes with 1,1,1-trifluoro-1′,1′,1′-trimethyl-4,4′-ethane-1,2-diyldi-imino)*bis*(pent-3-en-2-one) in aqueous solution at concentrations of 0.02–0.12 mg/ml has been reported.[89]

For the gas chromatographic determination of iron(III), its complexes with hexadentate ligands—4,4′,4″-(neopentane-1,3,4-triyltri-imino)*tris*(pent-3-en-2-one) and 4,4′,4″-(cyclohexane-*cis*,*cis*-1,3,5-triyltri-imino)*tris*(pent-3-en-2-one)—were used.[88] It was possible to

detect down to 1×10^{-10} g of iron on a column (46 × 0.65 cm) with 3% Silicone OV-101 on Gas-Chrom Q at 200 °C using a flame ionisation detector.

Several studies have been published that are devoted to a comparison of the chromatographic properties of volatile nickel(II) complexes with ligands of analogous structure to β-diketones but containing S, O and O, N pairs as well as S, N [90-93] as donor atoms instead of two oxygen atoms. In these studies 25 compounds of four types were studied:



monothio-β-diketonates (MTBDK) β-aminovinylketonates (AVK) β-aminovinylthionates (AVT)

The terminal groups in the compounds investigated were CH_3, CF_3, $H(CF_2)_2$, $H(CF_2)_4$, C_3H_7, C_2F_5, $C(CH_3)_3$, $CH(CH_3)_2$, n-C_4H_9, and C_6H_5 in different combinations. The complexes obtained were chromatographed on glass columns (1 m × 3 mm) using a constant recombination rate detector. Tests on different packings showed that the best results were given by Chromatone N-Super with 3% Silicone SE-30. Retention of all the chelates studied increased with an increase in the length of alkyl terminal groups and also when CF_3 was replaced by $H(CF_2)_2$. Introduction of a *tert*-butyl group improved the chromatographic properties of all the complexes. Complexes with phenyl substituents were not eluted at all or were eluted with a very long retention time.

Nickel monothio-β-diketonates were eluted at 190–210 °C giving asymmetric peaks in all cases. Aminovinylketonates had greater volatility than the corresponding MTBDK complexes and were eluted from the same column at 140–160 °C. Under the experimental conditions, AVK complexes that contained a fluoroalkyl substituent on the carbon atom bonded to the amino group had better chromatographic properties than their structural analogues containing an amino group joined to a carboxyl carbon atom. In several cases the characteristic abnormal behaviour of chelates on a column occurred. Despite their lower elution temperature, in most cases the nickel AVK proved to be less stable during gas chromatography than the MTBDK complexes. Nickel AVT had the best chromatographic properties. Like MTBDK, they were eluted at high temperatures (in the region of 200 °C), but they displayed virtually no abnormal effects and gave symmetrical peaks. The detection limit for these chelates reached 2.5×10^{-10} g.

In one study[94] the thermal stability and chromatographic behaviour of complexes of copper, nickel, zinc, cadmium, platinum, and palladium with 4,4'-(ethane-1,2-diyldi-imino)*bis*(pent-3-ene-2-thione) and copper and nickel complexes of 4-[(3-oxo-1-methylbut-1-enyl)-aminoethylamino]-pent-3-ene-2-thione were studied and the possibility of simultaneous gas chromatographic determination of copper, nickel, and zinc as such complexes was demonstrated. Out of the compounds studied only the cadmium complex proved to be thermally unstable.

V. GAS CHROMATOGRAPHIC SEPARATION OF METAL CHELATES ON CAPILLARY COLUMNS

Although the gas chromatography of metal chelates has been in existence for over 30 years, the first studies on the separation of chelates on capillary columns were only published in 1979. This may have been due to the lack of success in the early attempts to use metal capillary columns for this purpose. There is nothing surprising in this as even when glass and quartz capillary columns, which are much more inert in the chemical sense, are used it is only possible to chromatograph some of the most stable β-diketonates—chelates of chromium, aluminium, beryllium, copper, and a few other metals. The range of metal dialkyldithiocarbamates that can be separated on capillary columns is more extensive, which is probably due to their kinetic stability. Recently, some dialkyldithiophosphates and metal complexes with Schiff bases and porphyrins have also been separated by this method.

The methods used to separate metal chelates on capillary columns are virtually the same as those used for other high-boiling compounds. The most successful results are obtained on columns of length 5–15 m with polysiloxane deposited or grafted stationary phases. Injection of the sample is carried out both directly into the column and with split flow. A flame ionisation detector is usually employed.

The separation of structural isomers of chromium trifluoroacetylacetonates and mixed ligand complexes of chromium with TFA and HFA as well as a number of copper β-ketoaminates and cyclopentadienyl compounds of manganese and chromium on capillary columns made of stainless steel with a porous layer has been described.[95] Dexsil-300 was used as the stationary phase. The separation of aluminium, beryllium, chromium, and copper trifluoroacetylacetonates has been carried out on glass and quartz capillary columns of length 5–15 m.[96] Sievers and Brooks[97] separated 25 isomeric chromium β-diketonates on a quartz capillary column (30 m × 0.32 mm) with Silicone SE-54.

The chromatographic behaviour of trifluoroacetylacetonates, pivaloyltrifluoroacetonates, and trifluoroacetylisovalerylmethanates of aluminium, beryllium, chromium, copper, cobalt, iron, and nickel has been studied on quartz capillary columns with OV-101, OV-17, and SE-54.[98] In particular, it was possible to separate isomeric aluminium and chromium pivaloyltrifluoroacetonates. The detection limits of the metals when using a flame ionisation detector reached 4×10^{-14}–2.2×10^{-12}g.

The first successful attempt to separate rare earth β-diketonates on the glass capillary column has been reported.[99] Rare earth chelates with PTA were separated on a column (9.5 m × 0.3 mm) with OV-17 stationary phase and a programmed temperature increase (15 K/min) in the range 175–250 °C. It was possible to separate mixtures of Sc–Lu–Er–La, Sc–Lu–Tm–Ho–La, and others. When longer columns were used and silicones SE-30, OV-101, and SE-52 were employed as liquid phases, separation was less good.

The separation of DADTC complexes of iridium, palladium, lead, cadmium, zinc, selenium, rhodium, cobalt, and arsenic was carried out on a glass capillary column (7 m × 0.3 mm) with Silicone OV-101 at 190–255 °C.[100] A flame ionisation detector was used. An attempt to use pyrrolidinedithiocarbamates proved unsuccessful. The use of dipropyl- and dibutyl-dithiocarbamates gave better results;[101] it was possible to separate selenium, zinc, lead, and palladium chelates with a programmed temperature increase (20 K/min) in the range 170–245 °C. Calibration curves remained linear over the range 5×10^{-8}–1×10^{-6} g of chelate. When the content of chelate in the sample was less than 5×10^{-8} g, partial irreversible adsorption on the column occurred.

In one study[102] the chromatographic behaviour of DTFEDTC and di-isobutyldithiocarbamates of nickel, copper, zinc, cadmium, mercury(II), lead(II), and cobalt(III) was investigated. Separation was carried out on short (1–7 m) quartz and glass capillary

columns of internal diameter 0.30–0.32 mm with OV-101, SP-2100 and FFAP as liquid phases using different modes of programmed temperature increase. The best results were obtained when non-polar silicone liquid phases were used. Partial decomposition on the columns was only observed for the zinc chelates. The possibility of gas chromatographic detection of trace amounts of these metals was demonstrated.

More recently the determination of nickel, copper, and cobalt as their di-isobutyldithiocarbamates on capillary columns (3–4 m × 0.3 mm) with silicones SE-52 and SE-54 and a programmed temperature increase from 220–270 °C (30 K/min) has been reported.[103] The detection limits were $2-4 \times 10^{-11}$ g of metal. The method was used to determine metals in sea and tap water.

Sucre and Jennings[96] chromatographed different volatile metal complexes, including DEDTC and DTFEDTC complexes of zinc, copper, nickel, lead, and cobalt. Detection was carried out using flame ionisation, electron capture, flame photometric, and nitrogen phosphorus detectors. Separation was carried out on quartz and glass capillary columns of length 5–15 m with SE-30, SE-52, SE-54, SP-2100, Dexsil-300, and Carbowax 20 M as liquid phases. The best results were obtained on the silicone phases and on Dexsil. When an electron capture was used for the DTFEDTC complexes and a nitrogen phosphorus detector used to determine nitrogen, a sensitivity of $0.2-1.4 \times 10^{-12}$ g/sec was attained, when a flame photometry detector was used to determine sulphur the sensitivity was $0.7-1 \times 10^{-12}$ g/sec.

The determination of trace amounts of zinc, copper, cadmium, mercury, lead, and cobalt as DTFEDTC complexes using capillary glass chromatography at 90–250 °C on Silicone SE-30 with a flame ionisation detector has been reported.[104] The chromatographic behaviour of DTFEDTC complexes of thallium, mercury(II), cadmium, copper, cobalt, nickel, iron, lead, indium, bismuth, palladium, and zinc on glass and quartz capillary columns with Silicone SE-54 and on a capillary column with a chemically grafted phase of DB-5 has been investigated.[105] In one experiment the authors succeeded in separating complexes of thallium, zinc, copper, nickel, cadmium, palladium, cobalt, iron, indium, lead, and bismuth.

Chromatography of small quantities ($3-12 \times 10^{-8}$ g) of DEDTC and DTFEDTC complex of zinc, cobalt, lead, palladium, nickel, and copper on a short quartz capillary column (4.5 – 0.32 mm) with Silicone SE-54 has been carried out.[106] A flame ionisation detector was used. Dipropyl- and di-isobutyl-dithiocarbamates were also studied. Experiments were also carried out using a longer column (15 m), and the temperature was increased to 320 °C by programming. For the non-fluorinated chelates, in most cases it was only possible to obtain satisfactory chromatograms on the short column, and there was no advantage in using dipropyl and di-isobutyl derivatives. When separation was carried out on the long column, satisfactory peaks were obtained only for zinc and nickel DEDTC. The peak from bismuth DEDTC had a distorted shape in all cases.

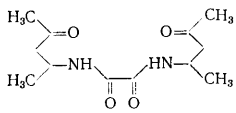
Nanogram quantities of zinc, copper, nickel, palladium, cobalt, chromium, and iron as their DTFEDTC complexes were determined on capillary columns.[107] The metals were extracted from aqueous solution at pH 3.5 with a solution of the ligand in chloroform. The sample was injected into a quartz capillary (5 m × 0.32 mm) installed before the column (15 m × 0.32 mm) with polymethylsiloxane as liquid phase. The column temperature was increased in the range 64–260 °C using a complex program. C_{20} and C_{24} hydrocarbons or palladium chelate were used as internal standards. The calibration curve for the chromium chelate was linear over the range $0.2-20 \times 10^{-9}$ g.

The separation of nickel(II), palladium(II), and platinum(II) DEDTC on a glass capillary column was achieved.[80]

Scheller and Neeb[108] detected chromium, nickel, copper, zinc, cadmium, and cobalt as their DTFEDTC complexes down to 1×10^{-9} g/ml using a flame ionisation detector. When an electron capture detector was used it was possible to improve the sensitivity further by a factor of 100, but the detector used was not adapted to work with capillary columns and as a result the peaks were considerably broken.

A method for the determination of small quantities of copper and nickel DEDTC on a glass capillary column has been reported, and it was characterised by having a large sample (10 μl) injected into a deactivated glass capillary (6 m × 0.32 mm) installed before the column.[109] Normal C_{22} alkane was used as the internal standard. The calibration curves retained linearity over the range $0.25-10 \times 10^{-9}$ g of chelate.

The behaviour of copper, nickel, palladium(II), and vanadyl chelates with a number of tetradentate β-ketoamines including a new type of ligand (tetraketone):



was studied on quartz capillary columns of length 25 m and 6.3 m (internal diameter 0.32 mm) with OV-101, OV-17, PEG-20 M as liquid phases and BP-1, BP-10, and BP-20 chemically grafted phases at 150–240 °C, as well as on packed columns with Silicones SE-30, OV-3, OV-17, OV-25, OV-210, and Dexsil-300 at 200 °C.[110] The best results were obtained on the OV-3 and OV-25 phases. The most suitable carrier gas to use for the capillary columns was hydrogen, which made it possible to work with quite good efficiency at high flow rates. The detection limits for the packed columns using a flame ionisation detector reached $100-140 \times 10^{-9}$ g of chelate, while for the capillary columns the limits were $0.2-2 \times 10^{-9}$ g of chelate. When nitrogen was used as the carrier gas the detection limits were higher by about a factor of 10.

More recently the behaviour of 17 chelates of copper, nickel, zinc, cadmium, platinum, palladium, and vanadyl with a number of tetradentate β-ketoamines and β-aminovinylthiones [111] were studied on five different capillary columns. The rate constants for decomposition of the chelates on the columns were determined along with other parameters. Their values varied from 10^{-1} to 10^{-3} sec^{-1} for the relatively unstable aminovinylthionates and were as low as 10^{-5} sec^{-1} for the stable β-ketoaminates. Enthalpies of solution were also determined for a number of chelates on several different liquid phases.

The gas chromatographic separation of complexes of nickel, copper, vanadyl, and cobalt(II) with etioporphyrin I and octaethylporphyrin has been reported for the first time.[112] Separation was carried out on a quartz capillary column (6 m × 0.3 mm) with Silicone OV-1 and a programmed temperature increase from 60 to 300 °C followed by exposure to an isothermal system. It was also possible to chromatograph porphyrin complexes of zinc, palladium-(II), titanyl, and platinum(II) under similar conditions. Satisfactory results were obtained when a glass column (10 m × 0.3 mm) with CP Sil S as liquid phase was used. The separation of complexes of silicon, aluminium, gallium, rhodium(III), and nickel with octaethylporphyrin, etioporphyrin I, and etioporphyrin III under similar

conditions was subsequently reported.[113] Metalloporphyrin complexes are the least volatile of all those used up to now in the chromatography of metal complexes with organic ligands, their separation was only achieved because of their excellent thermal stability and by using short capillary columns. It is probably true that because of the difficult quantitative conversion of metal ions to porphyrin complexes, at the present time the use of the latter for practical analysis cannot be considered.

VI. GAS CHROMATOGRAPHY OF METAL β-DIKETONATES IN LIQUID VAPOUR

The studies initiated in 1971 by Fujinaga et al.[114] on the chromatography of metal β-diketonates using a carrier gas with vapour from the corresponding β-diketone added (this method is usually not quite correctly called gas chromatography in ligand vapour—GCLV) have undergone further development. Thus, the determination by GCLV of trace amounts of beryllium as its trifluoroacetylacetonate in aluminium and its alloys with magnesium has been reported.[43] Analysis was carried out on a glass column (90 × 0.3 cm) filled with 0.5% Silicone SE-30 on glass beads at 130 °C. The carrier gas was argon with 0.05% TFA added, and a plasma detector with electrodeless discharge was used. The detection limit reached 1×10^{-12} g of beryllium. A similar method[115] was used to determine traces of copper and aluminium in metallic zinc.

A short communication[116] reports for the first time the complete separation of trifluoroacetylacetonates of four neighbouring rare earth elements (gadolinium, terbium, dysprosium, and holmium) on a column with a mixture of 0.2% PEG-20 M and 1.8% Silicone OV-17 on Chromosorb W at 240 °C. The gas carrier was helium with an extremely high concentration (10%) of TFA vapour, and a katharometer detector was used. Unfortunately, the column length was not stated in the study.

The separation of hexafluoroacetylacetonate adducts of rare earth radionuclides with TBP and TOPO on a column (2 m × 2.4 mm) with 2% polyphenyl ether or 3% Dexsil-300 on Chromosorb W has also been reported.[117] The carrier gas was saturated with HFA vapour at 60 °C. The column temperature was programmed to increase from 150 to 215 °C (8 K/min). A chromatogram which indicates the satisfactory separation of ten rare earth adducts over a period of 8 minutes was shown in the study.

The chromatographic behaviour of nickel and a number of other metal chelates with TFA under GCLV conditions has been studied[118] and a method for determining nickel in steel has been reported. Lead, cadmium, tellurium, molybdenum, and tungsten interfered with the determination. The determination of palladium as its trifluoroacetonylacetonate in the other metals of the platinum group using GCLV has been reported.[119] Other studies[27,120–122] have also been devoted to the application of GCLV.

When a chelate of europium with PTA was chromatographed in carrier gas containing acetylacetone vapour, ligand exchange occurred and less volatile mixed chelates were formed, containing PTA and AA anions.[27] A similar phemenon was found when an adduct of europium β-diketonate with TBP was chromatographed. When ligand vapour (HFA) was introduced into the carrier gas (1.6×10^{-6} g/ml) it was possible to obtain symmetrical peaks of hexafluoroacetylacetonate adducts of americium, curium, europium, terbium, and lutetium with TBP on a column with 5% Silicone SE-30 on Chromatone N AW DMCS at 205 °C.[122] The detection limits reached 5×10^{-8} g for americium and 3×10^{-9} g for curium.

The separate determination of manganese(II) and (III) ions in aqueous solution as chelates with TFA using GCLV has been reported.[123] One study[124] examines trifluoroacetylacetonates of chromium, aluminium, and iron by means of GCLV. Addition of TFA vapour to the carrier gas without exception improved the calibration curves of all the chelates, even that of the most stable chromium chelate.

VII. BEHAVIOUR OF METAL CHELATES ON A CHROMATOGRAPHY COLUMN

The abnormal effects that occur when the β-diketonates of many metals are chromatographed have been of interest to reseach workers for a long time. Among these effects are the irreversible adsorption of the first samples of chelate on a new column, the "memory" effect of a column, the "disappearance" of small samples of chelate on a column, the abnormal broadening of peaks, and so on. These phenomena have been described in detail in, for example, one monograph.[18] Berezkin[125] showed that such effects are the partial manifestations of general characteristics of the chromatographic process complicated by an appreciable degree of irreversible or quasi-irreversible chemisorptive interaction beween the components being separated and the column packing. In the case of metal complexes such as β-diketonates this type of interaction is likely to occur mainly with elimination of one ligand from the complex to give a free β-diketone molecule and is accompanied by attachment of the residue of complex to the matrix (solid support or liquid phase):

$$ML_n + HA \rightarrow ML_{n-1}A + HL$$

where M is metal, L is ligand, H is mobile hydrogen, A is matrix, and HL is free β-diketone.

This hypothesis, which was proposed some time ago,[18] was supported experimentally for the first time in one study,[126] where it was shown that rare earth dipivaloylmethanates were adsorbed on the column as cation complexes containing two ligand molecules.

The abormal effects mentioned above have been investigated in detail on copper(II) trifluoroacetylacetonate as a model.[127,128] A study of the distribution of copper chelate adsorbed on the column using a ^{64}Cu radioisotope showed that the adsorption depended on the quantity of chelate introduced, the content of the liquid phase, the nature of the solid support and the liquid phase, and the temperature. Considerable adsorption of chelate by wads of glass wool and fluoroplastic fibre holding the packing in the column was observed. The adsorption of chelate in the column was partly reversible.

More recently a similar study was published, being devoted to the chromatographic behaviour of zinc di(trifluoroethyl)dithiocarbamate[129] on a column, and it was carried out using a ^{65}Zn radioisotope. The authors also observed considerable adsorption of chelate on glass, quartz, and Teflon wool and indicated that the best results were obtained using metal gauze as wadding. To reduce the adsorption effects it was recommended to use glass and quartz capillarly columns rather than packed columns.

The interaction processes between metal β-diketonates and packing and with each other that occur on a column when the chelates of two different metals are chromatographed was studied by computer simulation.[130] The abnormal effects due to adsorption of hexafluoroacetylacetonate adducts of americium, curium, and some rare earth elements have also been described.[122]

Similar abnormal effects occurred when copper and iron β-diketonates were chromatographed on quartz capillary columns with different liquid phases. The partial oxidation of vanadium(III) chelate on a column to form vanadyl chelate was also observed. It is interesting to note that when nitrogen carrier gas was replaced by hydrogen the decomposition of the chelates in the column increased. Another study[132] is also devoted to the abnormal behaviour of metal β-diketonates on chromatographic columns.

VIII. GAS CHROMATOGRAPHIC DETERMINATION OF TRACE METALS

It is evident from what has been stated that the previous period of 11 years has been marked by considerable progress in the use of gas chromatography for practical analysis of trace amounts of metals. It is true that the limiting sensitivity of the method has not improved very much—the detection limit of most metals lies in the region of $10^{-11}-10^{-13}$ g per sample—and this is due to the absence of any noticeable improvement in the sensitivity of chromatographic detection in general. However, the total number of elements that can be determined with high sensitivity has increased substantially as a result of using new volatile complexes and the application of capillary columns.

A general Table featuring the present potentialities of gas chromatography in this field is given below.

Detection limits (m) of metals as volatile complexes using gas chromatography.

Metal	$m.10^{10}$.g	Refs.	Metal	$m.10^{10}$.g	Refs.
Be	0.0004	[133]	Ru	0.0024	[52]
Al	0.009	[134]	Rh	0.01**	[73]
Sc	0.03*	[135]	Pd	0.005**	[73]
V	0.085*	[135]	Ir	0.04**	[73]
Cr	0.00001	[34]	Pt	0.005**	[73]
Mn	500	[131]	Au	0.05**	[73]
Fe	0.13*	[135]	rare earths	200—300	[138]
Co	0.1	[136]	Cd	40	[63]
Ni	0.007	[137]	Tl	100	[105]
Cu	0.001	[137]	Pb	60	[63]
Zn	30	[63]	Hg	30	[63]
Ga	0.027*	[135]			

*Sensitivity of detection, $m'.10^{10}$ g/sec.

**Calculated on the basis of limiting dilution given in study.

REFERENCES

1. T.Kawamoto, Kagaku (Chemistry) (Japan), 1975, **30**, 727.
2. M.Mijazaki, Kagaku no ryoiki, (J.Japan Chem.), 1976, **30**, 144.
3. C.Burgett, Sepr. and Purific. Methods, 1976, **5**, **1.**
4. P.Uden and D.Henderson, Analyst, 1977, **102**, 889.
5. D.N.Sokolov, Uspekhi Khim., 1977, **46**, 740 [Russ. J. Chem. Rev., 1077(4).
6. P.Uden, Proc. Anal. Div. Chem. Soc., 1978, **15**, 4.
7. G.Schwedt, Top. Curr. Chem., 1979, **85**, 159.
8. Yu.S.Drugov, Zhur. Anal. Khim., 1980, **35**, 559.
9. P.Pathi and S.Pande, Chem. Era, 1982, **18**, 1.
10. P.Pathi and S.Pande, Metals and Miner. Rev., 1982, **21**, 51.
11. J.Maslovska and S.Starzynski, Wiad. Chem., 1982, **36**, 669.
12. R.Neeb, Pure and Appl. Chem., 1982, **54**, 847.
13. G.Nickless, J. Chromatogr., 1984, **313**, 129.
14. P.Uden, J.Chromatogr., 1984, **313**, 3.
15. V.Yu.Golubtsova, I.A.Murav'eva, and L.I.Martynenko, "Teoreticheskaya i Prikladnaya Khimiya β-Diketonatov Metallov" (Theoretical and Applied Chemistry of Metal β-Diketonates), Izd. Nauka, Moscow, 1985, p.173.
16. E.Uhlemann and R.Morgenstern, Z. Chem., 1977, **17**, 405.
17. Yu.S.Drugov, Zhur. Anal. Khim., 1985, **40**, 585.
18. D.N.Sokolov, "Gazovaya Khromatografiya Letuchikh Kompleksov Metallov" (Gas Chromatography of Volatile Metal Complexes), Izd. Nauka, Moscow, 1981, p.123.
19. G.Schwedt, "Chromatographic Methods in Organic Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1984, p.254.
20. V.P.Mikhailenko, I.P.Sereda, and A.N.Korol', Zhur. Anal. Khim., 1979, **34**, 862.
21. J.Maslovska and S.Starzynski, Chromatographia, 1983, **17**, 418.
22. J.Maslovska and S.Starzynskii, Mikrochim. Acta, 1984, **1**(5–6), 487.
23. B.A.Rybakova and M.A.Bondarenko, Zhur. Anal. Khim., 1984, **39**, 1428.
24. T.I.Astapova, O.D.Frolova, A.I.Kutepova, and L.V.Ovsynnikova, Zhur. Anal. Khim., 1984, **39**, 2179.
25. V.Yu.Golubtsova et al., Zhur. Neorg. Khim., 1981, **26**, 933 [Russ. J. Inorg. Chem., 1981(4)].
26. V.I.Spitsyn et al., Zhur. Neorg. Khim., 1982, **27**, 853 [Russ. J. Inorg. Chem., 1982(4)].
27. A.V.Davydov, E.V.Fedoseev, S.S.Travnikov, and B.F.Myasoedov, Radiokhim., 1980(4), 529.
28. D.N.Sokolov and G.N.Nesterenko, Zhur. Anal. Khim., 1975, **30**, 2377.
29. D.N.Sokolov and G.N.Nesterenko, "β-Diketonaty Metallov" (Metal β-Diketonates), Izd. Nauka, Moscow, 1978, p.81.
30. L.Jambor and R.Sievers, Proc. XVIII Int. Conf. on Coordination Chemistry, Sân Paulo, 1977, p.172.
31. A.Kito, M.Nakane, and V.Mijake, Bunseki Kagaku, 1978, **27**, 7.
32. S.Dilli and E.Patsalides, J. Chromatogr., 1979, **176**, 305.
33. G.N.Nesterenko and D.N.Sokolov, Zhur. Anal. Khim., 1979, **34**, 1958.
34. K.Buchtela, F.Grass, and G.Muller, J. Chromatogr., 1975, **103**, 141.
35. J.Lo and S.Yeh, J. Chromatogr. Sci., 1980, **18**, 359.
36. G.Hackey, J.Blais, and P.Klein, Anal. Chem., 1980, **52**, 1131.
37. G.Brubaker and J.Romberger, Inorg. Chem., 1980, **19**, 1087.
38. U.Bendig, H.Stenner, and A.Kettrup, Z. Anal. Chem.,1981, **309**, 370.
39. S.V.Volkov, L.E.Miropol'skaya, L.A.Mel'nikova, and E.A.Mazurenko, Ukr. Khim. Zhur., 1983, **49**, 682.
40. V.P.Mikahilenko and I.P.Sereda, "Teoreticheskaya i Prikladnaya Khimiya β-Diketonatov Metallov" (Theoretical and Applied Chemistry of Metal β-Diketonates), Izd. Nauka, Moscow, 1985, 197.
41. K.Komiya, T.Hayami, and S.Kawagichi, J. Hyd. Chem. (Japan), 1975, **21**, 3.
42. C.Kuo, I.Lin, J.Shih, and Y.Yeh, J. Chromatogr. Sci., 1982, **20**, 455.
43. T.Sakamoto, M.Okada, H.Kawaguchi, and A.Mizuike, Bunseki Kagaku, 1976, **25**, 85.

44. T.Gosink, Anal. Chem., 1975, **47**, 165.
45. D.Sokolov and G.N.Nesterenko, Zavod. Lab., 1976, **42**, 1172.
46. S.Dilli and E.Patsalides, Anal. Chim. Acta, 1981, **128**, 101.
47. R.Lovett and G.Lee, Environ. Sci, and Technol., 1976, **10**, 67.
48. M.Black and R.Sievers, Anal. Chem., 1976, **48**, 1872.
49. W.Wolf, Anal. Chem., 1976, **48**, 1717.
50. H.Tanaka, T.Nakano, and Y.Kanazawa, Bunseki Kagaku, 1983, **32**, 740.
51. G.Hawn, C.Talley, and A.Brown, Anal. Chim. Acta, 1981, **127**, 223.
52. S.Prescott and T.Risby, Anal.Chem., 1978, **50**, 562.
53. T.A.Bol'shova, Yu.S.Nikitin, E.N.Shapovalova, and M.B.Viryasov, Zhur. Anal. Khim., 1984, **39**, 1786.
54. T.O'Brien and J.O'Laughlin, Talanta, 1976, **23**, 805.
55. E.A.Mazurenko, Zn.N.Bublik, and S.V.Volkov, "β-Diketonaty Metallov" (Metal β-Diketonates), Izd. Nauka, Moscow, 1978, p.90.
56. K.Hellmuth and H.Mirzai, Z. Anal. Chem., 1985, **321**, 49.
57. K.Hellmuth and H.Mirzai, Z. Anal. Chem., 1985, **321**, 124.
58. G.D'Ascenzo and W.Wendlandt, J. Therm. Anal., 1969, **1**, 423.
59. A.Tavlaridis and R.Neeb, Z. Anal. Chem., 1976, **282**, 17.
60. J.Krupcik, J.Garaj, S.Holotik, et al., J. Chromatogr., 1975, **112**, 189.
61. A.Tavlaridis and R.Neeb, Naturwiss, 1976, **63**, 146.
62. A.Tavlaridis and R.Neeb, Z. Anal. Chem., 1976, **282**, 17.
63. M.Ahmad and A.Aziz, J.Chromatogr., 1978, **152**, 542.
64. A.Radecki, J.Halkiewicz, J.Grzybowski, and H.Lamparczyuk, J.Chromatogr., 1978, **151**, 259.
65. A.Radecki and J.Halkiewicz, J. Chromatogr., 1980, **187**, 363.
66. J.Krupcik, A.Lecler, J.Masaryk, and J.Garaj, J.Chromatogr., 1979, **171**, 604.
67. A.Joshi and R.Neeb, Z. Anal. Chem., 1986, **303**, 389.
68. A.A.Filatova and V.M.Byr'ko, "Khimicheskie Metody Analiza Promyshlennikh Materialov" (Chemical Methods for the Analysis of Industrial Materials), Moscow, 1983, p.143.
69. H.Schaller and R.Neeb, Z. Anal. Chem., 1986, **323**, 469.
70. A.Meyer and R.Neeb, Z. Anal. Chem., 1982, **113**, 221.
71. A.A.Filatova, "Materialy Konferentsii Molodykh Uchenykh" (Data from the Conference of Young Scientists), Khim. Fakul'tet MGU, Moscow, 1983, p.175; Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 28.12.83, No.7085-83.
72. J.Chovancova, J.Krupcik, and J.Garaj, Coll. Czech. Chem. Comm., 1984, **49**, 197.
73. K.Kritsotakis and H.Tobschall, Z. Anal. Chem., 1985, **320**, 152.
74. J.Halkiewicz. H.Lamparaczyk, and A.Radecki, Z. Anal. Chem., 1985, **320**, 577.
75. N.Carvojal and R.Zienius, J. Chromatogr., 1986, **355**, 107.
76. A.Kleinmann and R.Neeb, Z. Anal. Chem., 1977, **285**, 107.
77. B.Flegler. V.Gemmer-Colos, A.Deneks, and R.Neeb, Talanta, 1979, **26**, 761.
78. K.Yoshida, Y.Shimoishi, and K.Toei, Bunseki Kagaku, 1982, **31**, 276.
79. T.Cardwell, P.Marriott, and P.McDonough, J. Chromatogr., 1980, **193**, 53.
80. P.Marriott and T.Cardwell, J. Chromatogr., 1982, **234**, 157.
81. P.Uden and B.Waldmen, Anal. Lett., 1975, **8**(2), 91.
82. A.Kito, M.Nakane, and Y.Miyake, Bull. Govt. Ind. Inst. Osaka, 1977, **28**, 225.
83. A.Kito, M.Nakane, and Y.Miayke, Bull. Govt. Ind. Inst. Osaka, 1979, **30**, 291.
84. S.Dilli and E.Patsalides, J. Chromatogr., 1977, **130**, 251.
85. S.Dilli and E.Patsalides, Anal Chim. Acta, 1981, **128**, 109.
86. S.Dilli and A.Maitra, J. Chromatogr., 1983, **254**, 133.
87. S.Dilli, A.Maitra, and E.Patsalides, J. Chromatogr., 1985, **318**, 350.
88. S.Dilli and E.Patsalides, J. Chromatogr., 1983, **270**, 354.
89. O.W.Lau and W.I.Stephen, Anal. Chim. Acta, 1986, **180**, 417.
90. L.I.Bazhenova, K.I.Pashkevich, V.E.Kirichenko, and A.Ya.Azikovich, Zhur. Anal. Khim., 1981, **36**, 410.
91. V.E.Kirichenko, L.I.Bazhenova, A.L.Nikol'skaya, and K.I.Pashkevich, Zhur. Anal. Khim., 1982, **37**, 289.
92. K.I.Pashkevich, L.I.Bazhenova, V.E.Kirichenko, and I.G.Busygin, Zhur. Anal. Khim., 1985, **40**, 1694.
93. K.I.Pashkveich, L.I.Bazhenova, and V.E.Kirichenko, "Teoreticheskaya i Prikladnaya Khimiya β-Diketonatov Metallov" (Theoretical and Applied Chemistry of Metal β-Diketonates), Izd. Nauka, Moscow, 1985, p.207.
94. E.Patsalides, B.Stevenson, and S.Dilli, J. Chromatogr., 1979, **173**, 321.
95. P.Uden, D.Henderson, F.DiSanzo, and R.Lloyd, J. Chromatogr., 1980, **196**, 403.
96. L.Sucre and W.Jennings, High Resolut. Chromatogr. and Chromatogr. Comm., 1980, **3**, 452.
97. R.Sievers and K. Brooks, Proc.IX Int. Mass Spectroscopy Conf. Vienna, 1982, Part C, 527.
98. S.Wang, F.Xu, C.Li, et al., Khuasyue Syuebao (Acta Chim. Sin), 1985, **43**, 518.
99. S.Wang and X.Wu, New Frontiers Rare Earth Science and Applications, Proc. Int. Conf. Beijing, 1985, **1**, 569.
100. M.Riekkola, O.Makitie, and M.Sunderberg, Kemia-Kemi, 1979, **6**, 525.
101. M.Riekkola, Mikrochim. Acta, 1982, **1**, 327.
102. M.Riekkola, Mikrochim. Acta, 1983, **2**, 381.
103. M.Riekkola and S.Juntto, Mikrochim. Acta, 1985, **3**, 265.
104. G.Hartmetz, R.Neeb, and J.Borneff, Naturwiss., 1981, **68**, 477.
105. G.Hartmetz, G.Scollary, H.Meierer, et al., Z. Anal. Chem., 1982, **313**, 309.
106. H.Meierer and R.Neeb, Z. Anal. Khim., 1983, **315**, 422.
107. H.Scheller and R.Neeb, Z. Anal. Khim., 1985, **320**, 658.
108. H.Scheller and R.Neeb, Z. Anal. Khim., 1986, **323**, 473.
109. M.Termonia, J.Walravens, J.Vandegans, and C.Neve, J. High Resolut. Chromatogr. and Chromatogr. Comm., 1986, **9**, 357.
110. E.Patsalides and K.Robards, J. Chromatogr., 1985, **350**, 353.
111. E.Patsalides and K.Robards, J. Chromatogr., 1986, **357**, 49.
112. P.Marriott, P.Gill, and G.Eglinton, J. Chromatogr., 1982, **236**, 395.
113. P.Marriott, P.Gill, and G.Eglinton, J. Chromatogr., 1982, **249**, 291.
114. T.Fujinaga, T.Kuwamoto, and S.Murai, Talanta, 1971, **18**, 429.
115. T.Sakamoto, H.Kawaguchi, and A.Mizuike, J. Chromatogr., 1976, **121**, 383.
116. T.Fujinaga, T.Kuwamoto, and T.Kimoto, Talanta, 1976, **23**, 753.
117. N.Greulich, U.Hickmann, N.Trautmann, and G.Herrmann, Z. Anal. Chem., 1986, **323**, 839.
118. T.Fujinaga, T.Kuwamoto, and K.Sugiura, Bull. Inst. Chem. Res. Kyoto Univ., 1980, **58**, 201.
119. K.Sugiura, Benseki Kagaku, 1982, **31**, 235.

120. A.V.Davydov, B.F.Myasoedov, E.V.Fedoseev, and S.S.Travnikov, "XII Mendeleevskii S"ezd po Obshchei i Prikladnoi Khimii. Referaty Dokladov i Soobshchenii" (Abstracts of Reports and Communications at the XIIth Mendeleev Conference on General and Applied Chemistry), Vol.1, Moscow, 1981, p.187.
121. E.Fedoseev, S.Travnikov, A.Davydov, and B.Myasoedov, Radiochem. and Radioanal. Lett., 1982, **51**, 271.
122. E.V.Fedoseev, S.S.Travnikova, A.V.Davydov, and B.F.Myasoedov, Radiokhim., 1983(4), 450.
123. T.Fujinaga, T.Kuwamoto, K.Sugiura, and N.Matsubara, Anal. Chim. Acta, 1982, **136**, 175.
124. M.Siu, M.Fraser, and S.Berman, J. Chromatogr., 1983, **256**, 455.
125. V.G.Berezkin, "Gazo-zhidko-tverdofazanaya Khromatografiya" (Gas-liquid-solid Phase Chromatography), Izd. Khimiya, Moscow, 1986, p.112.
126. N.V.Magazeeva, L.I.Martynenko, I.A.Murav'eva, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 1986(8), 1813.
127. D.N.Sokolov, A.V.Davydov, S.Yu.Prokof'ev, et al., "Stroenie, Svoistva i Primenenie β-Diketonatov Metallov" (The Structure, Properties, and Application of Metal β-Dikatones), Izd. Nauka, Moscow, 1978, p.109.
128. D.Sokolov, A.Davydov, S.Prokofyev, et al., J. Chromatogr., 1978, **155**, 241.
129. H.Meierer and R.Neeb, Z. Anal. Chem., 1983, **313**, 121.
130. D.N.Sokolov, V.P.Gurarii, and L.B.Davydova, "Teoreticheskaya i Prikladnaya Khimiya β-Diketonatov Metallov" (Theoretical and Applied Chemistry of Metal β-Diketonates), Izd. Nauka, Moscow, p.188.
131. S.Dilli, S.Miller, and K.Robards, J. Chromatogr., 1985, **324**, 75.
132. V.P.Mikhailenko, I.P.Sereda, and A.N.Korol', Zhur. Anal. Khim., 1979, **34**, 2260.
133. K.Eisentraut, D.Griest, and R.Sievers, Anal. Chem., 1971, **43**, 2003.
134. D.N.Sokolov, G.N.Nesterenko, and L.K.Golubeva, Zavod. Lab., 1973, **39**, 939.
135. R.Dagnall, T.West, and P.Whitehead, Analyst, 1973, **98**, 647.
136. L.Lui, J.Lui, and J.Cheng, Fenxi huaxue (Anal. Chem.), 1984, **12**, 439.
137. P.Uden, D.Henderson, and A.Kamalizad, J. Chromatogr. Sci., 1974, **12**, 591.
138. C.Burgett and J.Fritz, Talanta, 1973, **20**, 363.

Division of the Institute
of Chemical Physics,
USSR Academy of
Sciences, Chernogolovka