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THE GAS CHROMATOGRAPHY OF β-DIKETONATES

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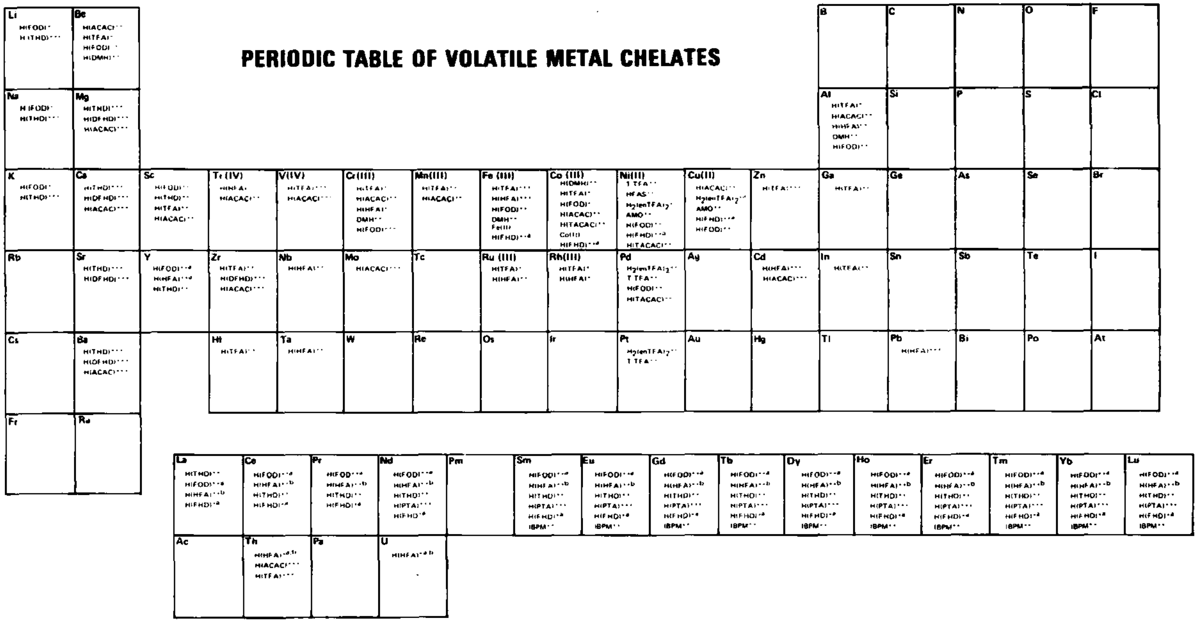
Since the initial studies of James and Martin[1,2], gas chromatography has revolutionized separations in organic and biochemistry. The development of the gas chromatography of metallic species has been relatively slow in coming; however, the inherent advantages of extraordinary sensitivity, speed and ease of separating mixtures of closely related compounds, has promoted a recent surge of interest in the technique. In general, gas chromatographs are not conveniently operated at temperatures in excess of 350° C. This temperature requirement places severe limitations on the types of inorganic compounds that can be chromatographed. In most, but not all cases, the metal complex must exhibit a vapor pressure of 0.1 to 1 mm of mercury in order to have a reasonable rate of gas-phase migration through the column[3]. To meet the requirement, the complexes must be unusually volatile and thermally stable in the chromatographic column. Metal compounds of suitable volatility are limited in number and include metal alklys, metal alkoxides, metal carbonyls, metal hydrides, metal halides, π-bonded metal complexes and β-diketonates. Furthermore, the compounds must be formed in quantitative yield to be of practical analytical utility. The metal halides and the metal β-diketonates are the only two of the above which meet all these requirements.

Pommier[4] has reviewed the determination of inorganic halides by gas chromatography up to 1966 and Anvaer and Drugov[5] have reviewed the literature from 1963 to 1970. Although many techniques have been developed and employed, the utility of metal analysis as metal halides is limited by the difficulty in synthesis and sample handling. By far the greatest chromatographic success has been achieved using metal β-diketonates as the volatile species. Research in this area has grown at such a rate as to have produced one book[6] completely dedicated to the subject and an entire chapter in a second[7]. In addition six review articles[8,9,10,11,12,13] have been published since 1966.

The volatility of metal acetylacetonates was first described by Morgan and Moss in 1941[14]. In 1955 Lederer[15] first suggested gas chromatography of metals as chelates of acetylacetone, but it was not until 1959 that Duswalt[16] actually chromatographed the acetylacetonates of berylium, zinc and scandium. Simultaneously, Biermann and Gesser[17] reported the successful elution of berylium, aluminum and chromium as complexes of acetylacetone. Although some success was achieved, the majority of the acetylacetonates are not sufficiently volatile and thermally stable to be chromatographed in the gas phase. In 1963 Sievers et al.[18] published a paper describing the gas chromatography of several metal chelates of acetylacetone H(ACAC), trifluoracetylacetone H(TFA) and hexafluoracetylacetone H(HFA). This paper was noteworthy in that it demonstrated a remarkable increase in volatility of the chelates of the fluorinated ligands. This increase in volatility on fluorination has been attributed to a reduction in van der Waals forces and a decrease in intermolecular hydrogen bonding[18].

Since 1963 the range of chelates of the β-diketonates which have been chromatographed has grown rapidly. A complete listing of the metals which have presently been studied is presented in Figure 1. A single asterisk marks complexes which have been determined quantitatively. The complexes with two asterisks have been eluted without apparent evidence of decomposition, and those with three asterisks produced chromatographic peaks, but there is evidence of some decomposition. The superscript "a" denotes complexes which have been eluted as mixed-ligand complexes with di-n-butylsulfoxide, DBSO. A superscript "b" indicates mixed-ligand complexes of tri-n-butylphosphate, TBP and the superscript "c" refers to the complex $MoO_2(ACAC)_2$.

It is apparent from this figure that virtually every metal capable of forming a complex with an oxygen donor has been studied by gas chromatography. Only those complexes which have completely filled coordination spheres or ligands which sterically restrict hydration have been successfully eluted without decomposition. The greatest success in gas chromatographic analysis has been realized for chelates of the small elements, berylium and aluminum and the extremely inert chromium diketonates.



PERIODIC TABLE OF VOLATILE METAL CHELATES

Li H(FOD)* H(THD)***	Be H(ACAC)** H(TFA)* H(FOD)* H(DMH)**											B	C	N	O	F
Na H(FOD)* H(THD)***	Mg H(THD)*** H(DFHD)*** H(ACAC)***											Al H(TFA)* H(ACAC)** H(HFA)** DMH** H(FOD)**	Si	P	S	Cl
K H(FOD)* H(THD)***	Ca H(THD)*** H(DFHD)*** H(ACAC)***	Sc H(FOD)** H(THD)** H(TFA)** H(ACAC)**	Ti (IV) H(HFA) H(ACAC)**	V(IV) H(TFA)*** H(ACAC)***	Cr(III) H(TFA)* H(ACAC)** H(HFA)* DMH** H(FOD)***	Mn(III) H(TFA)** H(ACAC)**	Fe (III) H(TFA)*** H(HFA)*** H(FOD)** DMH** Fe(II) H(FHD)**a	Co (III) H(DMH)** H(TFA)* H(FOD)* H(ACAC)** H(TACAC)** Co(II) H(FHD)**a	Ni(II) T TFA** HFAS** $H_2(enTFA)_2$* AMO** H(FOD)** H(FHD)**a H(TACAC)**	Cu(II) H(ACAC)** $H_2(enTFA)_2$** AMO** H(FHD)**a H(FOD)**	Zn H(TFA)***	Ga H(TFA)**	Ge	As	Se	Br
Rb	Sr H(THD)*** H(DFHD)***	Y H(FOD)**a H(HFA)**a H(THD)**	Zr H(TFA)** H(DFHD)*** H(ACAC)***	Nb H(HFA)**	Mo H(ACAC)***	Tc	Ru (III) H(TFA)* H(HFA)**	Rh(III) H(TFA)* H(HFA)*	Pd $H_2(enTFA)_2$** T TFA** H(FOD)** H(TACAC)**	Ag	Cd H(HFA)*** H(ACAC)***	In H(TFA)**	Sn	Sb	Te	I
Cs	Ba H(THD)*** H(DFHD)*** H(ACAC)***		Hf H(TFA)*	Ta H(HFA)**	W	Re	Os	Ir	Pt $H_2(enTFA)_2$** T TFA**	Au	Hg	Tl	Pb H(HFA)***	Bi	Po	At
Fr	Ra															

La H(THD)** H(FOD)**a H(HFA)**b H(FHD)*a	Ce H(FOD)**a H(HFA)**b H(THD)** H(FHD)*a	Pr H(FOD)**a H(HFA)**b H(THD)** H(FHD)*a	Nd H(FOD)**a H(HFA)**b H(THD)** H(PTA)*** H(FHD)*a	Pm	Sm H(FOD)**a H(HFA)**b H(THD)** H(PTA)*** H(FHD)*a IBPM**	Eu H(FOD)**a H(HFA)**b H(THD)** H(PTA)*** H(FHD)*a IBPM**	Gd H(FOD)**a H(HFA)**b H(THD)** H(PTA)*** H(FHD)*a IBPM**	Tb H(FOD)**a H(HFA)**b H(THD)** H(PTA)*** H(FHD)*a IBPM**	Dy H(FOD)**a H(HFA)**b H(THD)** H(PTA)*** H(FHD)*a IBPM**	Ho H(FOD)**a H(HFA)**b H(THD)** H(PTA)*** H(FHD)*a IBPM**	Er H(FOD)**a H(HFA)**b H(THD)** H(PTA)*** H(FHD)*a IBPM**	Tm H(FOD)**a H(HFA)**b H(THD)** H(PTA)*** H(FHD)*a IBPM**	Yb H(FOD)**a H(HFA)**b H(THD)** H(PTA)*** H(FHD)*a IBPM**	Lu H(FOD)**a H(HFA)**b H(THD)** H(PTA)*** H(FHD)*a IBPM**
Ac	Th H(HFA)**a,b H(ACAC)*** H(TFA)***	Pa	U H(HFA)**a,b											

FIGURE 1.

Periodic Table of Volatile Metal Chelates

The ability of the central metal atom to expand its coordination sphere to numbers greater than twice the positive charge has caused chromatographers many problems particularly with the divalent transition metals and the lanthanides. For example, the majority of the tris-β-diketonates of the lanthanides are eight coordinate. After formation of the tris complex with the β-diketone ligands, the remaining vacant coordination sites are filled with the solvent in which the lanthanide resides. When these sites are filled with water, problems occur in the thermal stability and in the solvent extraction of lanthanide β-diketonates. Mitchell[19] has shown that hydrated lanthanide β-diketonates decompose during thermal analysis. The presence of water in the coordination sphere contributes to the thermal instability by promoting self hydrolysis of the complex at elevated temperature. This thermal decomposition makes it difficult to determine the tris-β-diketonates of the lanthanides by gas chromatography. Eisentraut and Sievers[20] reasoned that the most promising approach in obtaining anhydrous, stable, volatile complexes would be with ligands which were sufficiently bulky to offer steric interference to the formation of hydrates. With this goal in mind, they synthesized 2,2,6,6-tetramethyl-3,5-heptanedione, H(THD). Using H(THD) they were able to prepare solid, anhydrous chelates of the lanthanides and reported the first successful determination of the lanthanides by gas chromatography[20].

Springer, Meek and Sievers[21] synthesized the β-diketone 1,1,1,2,2,3,3-heptafluoro-7, 7-dimethyl-4, 6-octanedione, H(FOD) to increase the volatility and retain the steric interference required for the formation of anhydrous complexes. They prepared the solid lanthanide chelates as monohydrates and found them to be easily dehydrated under vacuum. These anhydrous chelates were successfully chromatographed and were much more volatile than the H(THD) chelates. No gas chromatographic separation or quantitative data were reported and lanthanum, cerium and praseodymium chelates were not eluted. As a resulted of these studies, Eisentraut and Sievers were granted two U.S. patents[22,23]. While these studies were impressive and contributed to the understanding of the undesireable chromatographic properties of hydrated complexes, very few analytical methods for metal analysis by gas chromatography had been developed.

In order to be suitable as an analytical method the sample preparation should be rapid, assist in isolation from interferences and be quantitative. The majority of the preparations of the metal chelates have been by direct synthesis. This technique is less than quantitative and requires sublimation for isolation and purification before injection. The technique for solvent extraction allows rapid preparation of a chelate in the organic phase ready for injection and chromatography. Many of the metals shown in Figure 1 can be readily extracted, however, some, such as the divalent transition metals and the lanthanides, are not easily extracted. The difficulty in the solvent extraction of metals is a result of the formation of hydrated complexes. This hydrophilic nature precludes efficient transfer to the organic phase in an extraction. Ferraro and Healy[24] found that an organic base such as tri-n-butylphosphate will displace water from the coordination sphere of the lanthanide complexes, thereby making the complexes hydrophobic and effecting a quantitative extraction. The research on mixed-ligand extraction, commonly referred to as synergic extraction, has been thoroughly reviewed by Cary[25] and Mitchell[19].

Mitchell[19] has recently completed a study of synergic extraction systems, employing fluorinated β-diketones and various organic donors. Several mixed-ligand complexes which were both volatile and quantitatively extracted were identified. Mitchell has shown that the formation of a mixed-ligand complex of the lanthanides in an extraction is represented by Equation 1.

$$M^{+3} + 3H(L)_o + nD_o = M(L)_3 \cdot nD_o + 3H^+ \qquad (1)$$

The subscripts (o) are used to indicate the organic phase. When the initial concentration of β-diketone, H(L), is kept constant and in excess and the concentration of H^+ is kept at a low level, (pH = 5.5), the equilibrium is dependent on the amount of neutral donor D. The extraction becomes quantitative when the stoichiometric amount of neutral donor is added. Mitchell also reported that symmetrical, fully fluorinated ligands, containing seven carbon atoms or more, possessed the best extraction properties.

Butts and Banks[26] were the first to apply mixed-ligand systems to the extraction and subsequent gas chromatographic determination of the lanthanides. The technique allowed direct preparation of anhydrous HFA-TBP chelates in the organic phase ready for injection into the gas chromatograph. Sieck[27] has studied several mixed-ligand systems and achieved successful elution of the lanthanides as mixed-ligand complexes.

Burgett[28] found that the symmetrical ligand 1,1,1,2,2,6,6,7,7, 7-decafluoro-3, 5-heptanedione could be used in combination with di-n-butylsulfoxide for the synergic extraction and subsequent separation of the lanthanides[28,29,30,31]. Subsequently Utsunomiya et al.[32] eluted the lanthanides as mixed-ligand complexes of pivaloyltrifluoracetone and tri-n-butylphosphate or trioctylphosphine oxide.

Synergic solvent extraction has also found utility in the preparation of stable complexes of cobalt (II), iron (II) and nickel (II)[33,34,35] and Sieck et al.[36] have reported the successful separation and quantitative determination of uranium and thorium as the HFA-DBSO mixed-chelates. Mitchell and Banks[37] have shown both $U(HFA)_4$ and $UO_2(HFA)_2TBP$ to be volatile and chromatographable.

Since the initial report of the gas chromatography of metal β-diketonates in 1963,[18] workers in the area have reported many non-ideal column phenomena. Frequent observations of column "loading" and the displacement[6,27,38,39,40,41,42] of previously studied complexes have beeen reported. The peak shape of the eluted species is commonly asymmetrical and the HETP realized is much higher than that found in studies of organic compounds of comparable volatility. This non-ideal column performance has been the limiting factor to the development of quantitative methods by gas-liquid chromatography (GLC). The nature of the partitioning of metal chelates on GLC columns has been studied by Veening and Huber[43], and Sieck[27]. They have reported the retention volume, V_{Rg}°, to be a function of partitioning of the metal chelates with the liquid phase, KV_L, and a function of adsorption by the solid support, k_sA_s. Unden and Jenkins[41] have suggested that displacement phenomena were also a result of interaction with the solid surface; however, precise experimental evidence was not presented to support this conclusion.

Recently a comprehensive study into these phenomena was reported[44]. The authors found that the retention volume for the mixed-ligand complexes of the lanthanides was a function of the liquid phase as well as the solid support involved. For polar liquid phases such as QF-1 at least three phenomena were contributing to the retention volume: (i) bulk partitioning with the liquid phase, KV_L; (ii) adsorption on the solid support, k_sA_s; and (iii) adsorption on the surface of the liquid phase, k_aA_L. For nonpolar phases such as SE-30 and Dexsil 300 GC the net retention volume of the mixed-ligand complexes was apparently a function only of the partitioning behavior of the complex with the liquid phase, KV_L, and adsorption on the solid support, k_sA_s.

Furthermore it was hypothesized that interaction with the bulk liquid by complexation or other forms of association may make an appreciable contribution to the retention observed when QF-1 was used as the liquid phase. This type of interaction is likely to occur when polar liquid phases are used and polar solutes chromatographed. Experimentally this results in chromatographic peaks which have sharp leading edges with long tailing edges. As shown in Figure 2, this peak assymmetry is observed when QF-1 liquid phase was used but not when Dexsil 300 GC was used as the liquid phase. The situation becomes more complicated for mixtures of metal chelates, where a sequence of adsorption, displacements and possibly further interaction and breakdown is involved.

This "loading" has been attributed to adsorption on the solid support[27]. Burgett and Fritz[44] reported an increase in "loading" required when polar liquid phases were used in addition to the "loading" on the uncoated support and have suggested the possibility of complexation with/or ligand stripping by the liquid phase. They also reported that with columns which exhibited liquid phase "loading" it was possible to observe chelate exchange when a new complex was injected after repeated analysis of another.

This exchange was expected to be quantitative. When the displacement behavior was observed chromatographically, the peaks had the same retention times

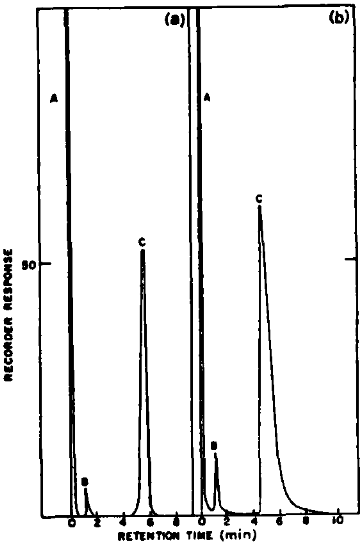


FIGURE 2.

Chromatograms of $Tb(FHD)_3 \cdot 2DBSO$, 20 x ¼ in. column, temperature 200°; liquid phase (a) 23.5% Dexsil, (b) 8.20% QF-1 A = cyclohexane-H(FHD), B = DBSO, C = $Tb(FHD)_3 \cdot 2DBSO$.

as the individual complexes. The constant retention time was explained if a uniform loading of the initial chelate occurred throughout the column. As the second chelate started through the column some of the previously loaded chelate was displaced. This deplacement begins at the injection port end of the column, then both complexes move down the column and are partitioned. Eventually all of the previously "loaded" complex was displaced (after several injections) and the column performs quantitatively for the new complex. This deplacement interaction was particularly bad when polar liquid phases were used and has been observed even with Teflon solid supports.

These non-ideal phenomena are observed to a lesser extent when Dexsil 300 GC is used as a liquid phase and when inert complexes are chromatographed. The value of preparing inert complexes cannot be minimized. By elimination of possible coordination sites, non-equilibrium interaction is diminished.

ANALYSIS OF CHELATES

Alkali Metals

The alkali metals generally form salts with acidic reagents rather than metallic complexes, however, some work has been reported on the gas chromatography of alkali metal chelates. Belcher et al.[45] reported the synthesis of derivatives of H(PHD) and H(FOD). The chelates of lithium, potassium and sodium were reported to be thermally stable and chromatographable with levels as low as 1 ng detected. Mass spectral studies confirmed the stoichiometry, but separations were not achieved because of ligand exchange[45].

Tetrakis mixed-metal complexes with the alkali metals and the lanthanides of the general type $M_t ML_4$ have also prepared[46] and are reported to be volatile, although gas chromatographic studies were not performed.

The monothio derivative of hexafluoroacetylacetone, H(THFA), has been reported[47] to form volatile chelates with sodium, however, actual chromatographic data has not been shown for this complex.

Alkaline Earths

With the notable exception of berylium, the successful gas chromatographic analysis of the alkaline earths has eluded researchers. Yamakawa[48] reported the successful synthesis of volatile acetylacetones of calcium, magnesium and barium but found that all decomposed on attempts at chromatographic analysis. Arakawa[47] reported excellent chromatography and separation of twelve hexafluoracetylacetonates, including magnesium, but, the composition of the eluted species was not confirmed. The chromatographic analysis of magnesium as the trifluoroacetylacetonate has also been reported[49] although no eluent identification was included.

Sievers and Schwarberg[50,51] have reported the synthesis and successful chromatography of H(THD) complexes with magnesium, calcium, barium and strontium. Elution of the individual complexes was achieved and confirmed by emission spectroscopy but mixtures of the pure chelates could not be separated. Studies of the elution products from these mixtures by mass spectroscopy were reported to reveal hetero-metallic species of the stoichiometry $M^1M^2(THD)_4$. This type of species has prevented analytical chromatography of the alkaline earths.

The analysis of berylium has been one of the most successful applications of metal chelates to gas chromatography. Berylium was one of the first chelates to be chromatographed by Duswalt[16]. Since 1959 berylium has been chromatographed as the acetylacetonate[52,53,54] , hexafluoroacetylacetonate[47], tetramethylheptanedionate[50,55,56], dimethylheptanedionate[57] and the thenoyltrifluoroacetonate[58]. While considerable success was achieved with the above systems, the greatest applications have been found using the trifluoracetylacetonates of berylium. These complexes are extremely stable, volatile and posses fluorine atoms which enable electron capture detection. Several workers[59,60,61,62,63,64] have studied the response of the electron capture detector and have found minimum detectible quantities as low as 4×10^{-13} g[61]. This exceptional sensitivity has allowed method development for the analysis of traces of berylium in air[38,65,66,67,154], blood[32,65,68,69,70] and urine[65,70,71]. In addition the analysis of the Apollo moon samples for berylium content was performed by gas chromatography[72,73]. Kawaguchi[74] has reported satisfactory response to berylium as the H(TFA) chelate using a plasma emission detector and this technique may see further development.

Group IIIA

All of the group IIIA metals except thallium have been studied by gas chromatography. Gallium as the (HFA)[47], HTFA[46,75,76,77], and H(ACAC)[54] derivatives and indium H(ACAC)[54], (HTFA)[76,77,78,79,80,81] and H(PTA)[57] derivatives generally show evidence of decomposition on chromatography. In spite of this fact, Morie and Sweet[77] have developed a solvent extraction gas chromatographic method for the analysis of aluminum, gallium and indium, and Schwarberg and Moshier[79] have quantitatively analyzed mixtures of aluminum, gallium, indium and berylium.

Because of their high thermal stability, the β-diketonates of aluminum have been the subject of considerable research[18,47,49,55,57,58,74,82,83,84]. Aluminum has been chromatographed and detected by the electron capture detector[39,40,60,85,86] and the flame photometric detector[87]. Aluminum has been determined in the presence of iron[88], iron and copper[76,89] and uranium[90,91]. Miyazaki and Kaneko[92] have developed a procedure for the trace analysis of aluminum in biological materials.

Group IVB

Considerable success has been achieved in the analysis of titanium, zirconium and halfnium by gas chromatography but as the chlorides, not the β-diketonates. Zirconium was one of the first acetylacetonates studied[16] but, as in succeeding attempts with H(TFA), H(HFA) and H(ACAC)[18,93], decomposition prevented analysis. Halfnium has also been studied[18,93] but it too proved unstable for gas chromatographic analysis. Titanium does not form volatile β-diketonato complexes.

Group VB

Vanadium is the only member of the group VB metals that can be chromatographed as the β-diketonato complex. Jacquelot and Thomas[58,94,95] have had considerable success in the analysis of thenoyltrifluoroacetone complexes of the vanadyl ion. Yamakawa[54] and Tackett[96] have also reported the successful chromatography of the vanadyl complexes with acetylacetone.

Group VIB

Tungsten forms no volatile chelates with the β-diketones and only one report[54] has been made concerning the unsuccessful attempt at the gas chromatography of $MoO_2(ACAC)_2$. On the other hand, considerable success has been achieved in the gas chromatographic analysis of chromium (III). Most of this outstanding success can be attributed to the ability of chromium to form extremely inert complexes. While chromium has been chromatographed as chelates with several β-diketones[17,18,40,47,48,56,58,82,85,97,98,153], the greatest success has been realized with trifluoroacetylacetone complexes[39,40,49,59,60,66,74,76,84,86,99,100,101,102,103,104,105,106,107,108,109,111,112,113]. The preparation of the H(TFA) complex is too slow for direct solvent extraction but can be performed by heating or radio frequency excitation of sealed vessels.

The electron capture detector has found wide application to the detection of ultratrace levels of chromium. The most notable of these has been in the analysis of chromium levels in blood and urine[99,100,101,103,108,109,110,111,112,113]. The flame photometric detector has been investigated as a detector for the analysis of chromium[87,104,105,106] with excellent sensitivity allowing detection of 79 picograms[101] as shown in Figure 3. Kawaguchi et al.[74] have also used a microwave emission detector with promising results for the analysis of chromium. Geometric isomers of $Cr(TFA)_3$ have been separated by gas chromatography[27,49,72,100,102,115] and other optical isomers of $Cr(HFA)_3$ have been resolved[115]

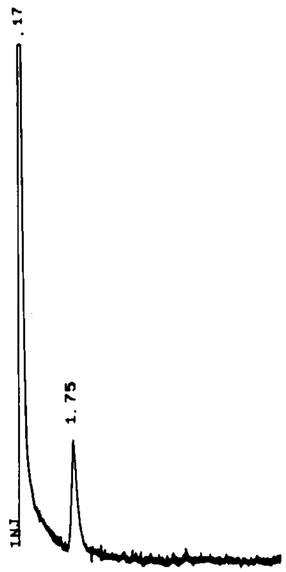


FIGURE 3.

Chromatogram of 79 picograms chromium, S/N of 12.6

Group VIIB

The only member of this group which has received the attention of chromatographers is manganese in the plus two oxidation state. Manganese has been studied as the H(ACAC) complex[54,96], the thenoyl complex[58], the H(HFA) complex[49]. In all cases successful elution, without decomposition, was not achieved.[49]

Group VIII

Considerable research has been spent on method development for these metals. Iron (III), copper(II), nickel(II) and cobalt(II) have all been chromatographed as diketonato complexes[18,46,47,55,56,57,58,60,76,84,95,97,114,116,117,118]. For the most part the complexes tend to form hydrates which readily decompose or are reversibly adsorbed by the column packing. A notable exception to this is the H(FOD) complex of cobalt (III) which has been successfully chromatographed at subnanogram levels[119]. In order to avoid this decomposition Moshier and Gere[89] prepared several amine adducts with H(TFA) and had limited success in the chromatography of cobalt (II) and nickel(II). Similar results were reported for dimethylformamide-H(TFA) mixed-ligand complexes of cobalt and nickel(II) by Jacquelot and Thomas[35]. Recently Burgett[33,34] combined synergic solvent extraction and gas chromatography to obtain the successful resolution of iron(II), nickel(II) and cobalt (II) as the mixed-ligand H(FHD) and DBSO complexes as shown in Figure 4. Ruthenium (III) has been separated from cobalt (II) as the H(HFA) chelate[120] and analyzed by electron capture detection. Several attempts have been made at the chromatography of rhodium[18,40,47,49] with good success being reported. Rhodium complexes have also been determined using the flame photometric detector[87,104,105].

As described above, many of these metals have been eluted as complexes with β-diketones but have shown signs of apparent decomposition. Apparently this decomposition is caused by the labile nature of the complexes. To form more stable complexes, Bayer et al.[121,122] synthesized the ligand 1,1,1,5,5,5-hexafluoro-2-hydroxylpent-2-en-4-thione, H(THFA) and successfully chromatographed the bis complexes of nickel, palladium and platinum. Belcher et al.[123] reasoned that complexes of the a-b type[85], that is those preferring both first and second row donor atoms, might form complexes of high stability with

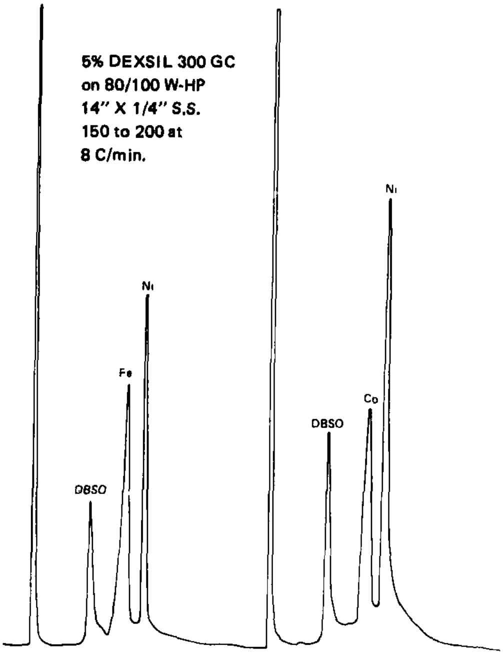


FIGURE 4.

Chromatograms showing the separation of Iron (II) and Co (II) from Ni (II). Conditions Temperature program 150°C to 220°C at 8° C/min.

sulfur donor ligands. To demonstrate this point, Belcher and co-workers[123,124 125,126,127,128] synthesized 1,1,1-trifluoro-2-hydroxylpent-2-en-4-thione, H(TTFA) and have reported separation of nickel, palladium and platinum and quantitative analysis for nickel. Stephen et al.[128] have also chromatographed cobalt, nickel and palladium H(TTFA) complexes.

Belcher and co-workers have found excellent success with bidentate β-ketoamine derivatives[126,130,131] and Uden and co-workers have developed ultratrace techniques for these complexes of nickel, copper and palladium[132,133, 134,135].

Group IB

With one exception, the gold hexafluoromonothioacetylacetonate complex[122], all the volatile complexes of these metals have been those of copper. Copper complexes with various β-diketones have been formed and attempts at the gas chromatography of the resultant chelates have been successful[18,47,49,51,54,55,56,57,60,81,85,86,95,116]. When attempts at trace level analysis have been made the complex rapidly loses chromatographic integrity. In an effort to circumvent this problem an attempt at the synthesis of mixed-ligand complexes of H(FHD) and DBSO was made[33,34]. Copper did not form the mixed-ligand species but was extracted and chromatographed as the bis-diketonate. This complex also showed adsorption and decomposition problems when low concentrations were injected.

Complexes of copper with nitrogen[122,130,131,132,133,134,135,136,137] and sulfur[122,126] containing ligands have met with better chromatographic success. Bayer et al.[122] has reported the synthesis of volatile H(HTFA) complexes and Belcher et al.[126] have chromatographed H(TTFA) complexes. By far the greatest success including ultratrace analysis has been achieved by Uden and co-workers[130,131,132,133,134,135] using bi and tetradentate keto-imine complexes. As shown in Figure 5 these complexes are extremely stable and show no adverse column properties in spite of the relatively low volatility.

Miyazaki et al.[136,137] have prepared copper and nickel chelates of some β-diketo-amine derivatives of H(ACAC) and salicylaldehyde, some of which are reported to be thermally stable. Richardson and Sievers[138] reported the synthesis of bis(hexafluoroacetylacetone)ethylenedi-imine and its copper complex but did not report any gas chromatographic studies.

Group IIB

The gas chromatography of these metals has been an unfruitful area. Yamakawa et al.[54] reported the elution, with decomposition of zinc and cadmium as the acetylacetonate complexes. Later Tanikawa et al.[49] chromatographed zinc trifluoroacetylacetone and reported sharp symmetrical peaks, however, eluent composition was not confirmed. Volatile and stable zinc H(THD) complexes have been studied by Sievers and Schwarberg[51] and Bayer et al.[122] and have reported the synthesis of volatile zinc and mercury hexafluoromonothioacetylacetonates but no gas chromatographic studies were performed.

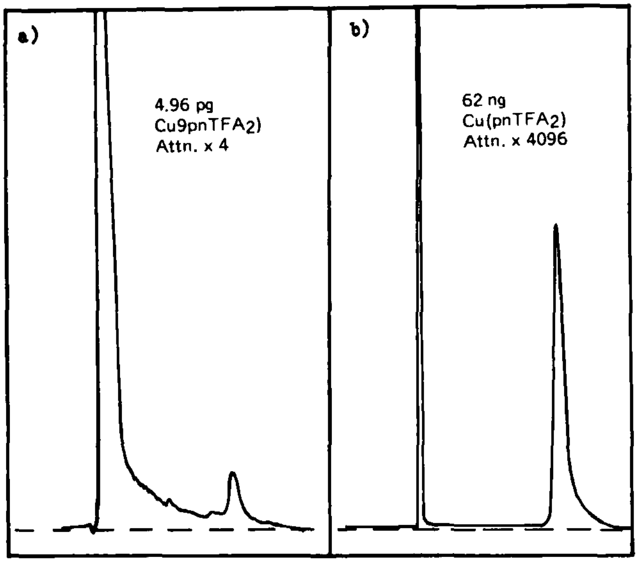


FIGURE 5.

Chromatograms (Hewlett-Packard Ni^{63} ECD) of $Cu(pnTFA_2)$. Column 3 ft. x 4 mm I.D. glass, 1.5% Dexsil 300 GC on Chromosorb W at 260°C.

Scandium, Yttrium and the Lanthanides

The volatile complexes of the lanthanides and scandium are of considerable interest to chromatographers. This interest has existed since the beginning of inorganic gas chromatography when Lederer[15] suggested the possibility of separation of the lanthanides as H(ACAC) complexes. The first chromatography of this family was performed by Duswalt[16] when he successfully eluted scandium acetylacetone. Since this time scandium has been successfully chromatographed as several β-diketonate complexes by numerous research groups[53,58,60,64,80,85,139,140,141]. Considerable interest in the gas chromatography of lanthanide β-diketonates has also been shown[14,20,21,22,32,46,52,53,57,78,143,144,145,146,147,148]. Separations were not achieved and low levels of the complexes could not be eluted.

As discussed above, this decomposition problem was related to the hydration of the lanthanide complexes. In 1970 Butts and Banks[26,182] reported that mixed-ligand complexes of H(HFA) and TBP had increased stability and achieved limited separations of the lanthanides. Subsequently Sieck[27,118] and Utsunomiya[149] investigated numerous mixed-ligand systems and achieved some resolution of the lanthanides. The first resolution of the lanthanides on an every other one basis, as shown in Figure 6 was reported by Burgett[28,29,30,31]. This system also proved unsuitable for trace level analysis.

The Actinides

Uranium and thorium as uranyl and as thorium (IV) have been successfully chromatographed β-diketonates. For the most part the complexes with

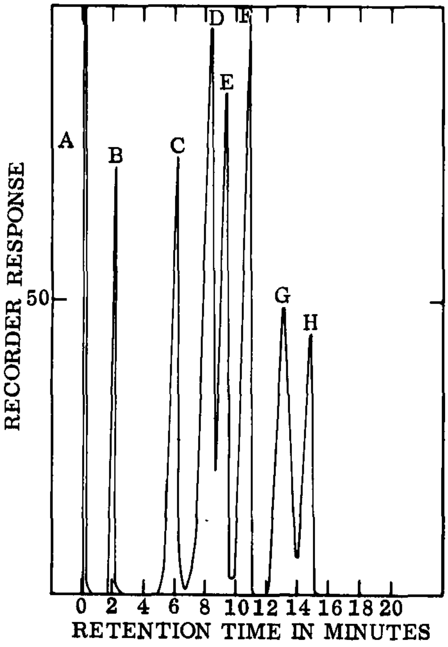


FIGURE 6.

Gas chromatogram of a mixture of FHD and DBSO mixed complexes of Yb, Er, Dy, Gd, Nd and Ce. 4 min hold at 172°C, temperature increase 4°/min. *A*-Cycloxhexane H(FHD); *B*-DBSO; *C*-Yb$(FHD)_3$ · 2DBSO; *D*-Er$(FHD)_3$ · 2DBSO; *E*-Dy$(FHD)_3$ · 2DBSO; *F*-Gd$(FHD)_3$ · 2DBSO; *H*-Ce$(FHD)_3$ · 2DBSO.

H(ACAC)[54], H(TFA)[49,60,84], H(FOD)[150] and trifuloropivaloylmethane[57] have shown signs of decomposition on chromatography. Mitchell found that uranyl and thorium complexes with H(HFA) could be quantitatively extracted as a volatile species when a mixed-ligand system was incorporated[37]. This synergic system of H(HFA)-TBP was further studied by Sieck[27] and resulted in a method for the separation and quantitative determination of uranium and thorium[36].

Lead

The successful determination of lead by the gas chromatography of volatile complexes has been the goal of many researchers in inorganic gas chromatography. Unfortunately this goal has not been achieved. Arakawa and Tanikawa have reported the chromatography of lead as the H(HFA) complex but no eluent identification or quantitation was reported. Belcher et al.[75] studied numerous lead β-diketonates by GC, TGA, and Mass Spectrometry but found that even the thermally stable chelates could not be quantitatively chromatographed due to strong column interaction. Recently Bayer et al.[122] reported the preparation of a stable, volatile lead complex with hexafluoromonthioacetylacetone but no chromatographic data was shown. Burgett[34] has studied the synergic solvent extraction of lead with H(HFD) and DBSO and found that rapid quantitative extraction could be achieved but the complex decomposed on chromatographic analysis.

Conclusion

As has been shown in the preceding paragraphs, the development of the gas chromatographic analysis of metal chelates has progressed admirably since its suggestion in 1955. Several exciting and useful analytical methods have already been developed and considerable research is still proceding. While many problems still remain the development of the technique of synergic solvent extraction, mixed-ligand complex chromatography, the synthesis of new heteroatomic ligands, and the advent of new liquid phases should soon increase the number of unique techniques for analysis of metals. With even a fraction of the scientific enginuity already demonstrated, it may well come to pass that the analysis of metals by gas chromatography will become as common as the gas chromatography of hydrocarbons.

References

1. A.T. James and A.J.P. Martin, Biochem. J. Proc., 48, 7 (1951).
2. A.T. James and A.J.P. Martin, Analyst, 77, 915 (1952).
3. R.E. Sievers in "Coordination Chemistry, Proceedings John C. Bailor Jr. Symposium", S. Kirschner ed., New York, New York, Plenum Press, 1969, pp. 270-88.
4. C. Pommier, Revue de Chimie Minerale, 3, 401 (1966).
5. B.I. Anvaer and Y.S. Drugov, Zh. Anal. Khim., 26, 1180 (1971).
6. R.W. Moshier and R.E. Sievers, "Gas Chromatography of Metal Chelates", New York, Pergamon Press, 1965.
7. G. Guiochon and C. Pommier, "Gas Chromatography in Inorganic and Organometallics", Ann Arbor Science Publisher, Inc., Ann Arbor, MI, 1973.
8. K. Arakawa and K. Tanikawa, Bunseki Kagaku, 15, 398 (1966).
9. R.S. Barratt, Proc. Soc. Anal. Chem., 10, 167 (1973).
10. P. Jacquelot and G. Thomas, Bull. Soc. Chim. France, 1261 (1973).
11. T. Kuwamoto, Bunseki Kagaku, 21, 445 (1972).
12. D.N. Sokolov, Zh Analit. Kim., 27, 993 (1972).
13. W.I. Stephen, Proc. Soc. Anal. Chem., 9, 137 (1972).
14. G.T. Morgan and H.W. Moss, J. Chem. Soc., 105, 189 (1914).
15. M. Lederer, Nature, 176, 462 (1955).
16. A.A. Duswalt, Disser. Abstr., 20, 52 (1959).
17. W.J. Biermann and H. Gesser, Anal. Chem., 32, 1525 (1960).
18. R.E. Sievers, B.W. Ponder, M.L. Morrie and R.W. Moshier, Inorg. Chem., 2, 693 (1963).
19. J.W. Mitchell, Ph.D. Thesis, Ames Iowa, Library, Iowa State University, 1970.
20. K.J. Eisentraut and R.E. Sievers, Amer. Chem. Soc., 87, 5254 (1965).
21. C.D. Springer, Jr., D.W. Meek and R.E. Sievers, Inorg. Chem., 6, 1105 (1967).
22. K.J. Eisentraut and R.E. Sievers, U.S. Patent 3,429,904, Feb. 25, 1969.
23. K.J. Eisentraut and R.E. Sievers, U.S. Patent 3,453,319, July 1, 1969.
24. J.R. Ferraro and T.V. Healy, J. Inorg. Nucl. Chem., 24, 1463 (1962).
25. M.A. Carey, Ph.D. Thesis, Ames, Iowa, Library, Iowa State University, 1967.
26. W.C. Butts and C.V. Banks, Anal. Chem., 42, 133 (1970).
27. R.F. Sieck, Ph.D. Thesis, Ames, Iowa, Library, Iowa State University, 1971.

28. C.A. Burgett, Ph.D. Thesis, Ames, Iowa, Library, Iowa State University, 1972.

29. C.A. Burgett, Presented at Mid-Atlantic Regional ACS Meeting, Jan. 14, 1973.

30. C.A. Burgett and J.S. Fritz, Anal. Chem., 44, 1738 (1972).

31. C.A. Burgett and J.S. Fritz, Talanta, 20, 363 (1973).

32. K. Utsunomiya and T. Shigematsu, Anal. Chim. Acta, 58, 411 (1972).

33. C.A. Burgett, Paper 87, 24th Pittsburgh Conference, March 6, 1973.

34. C.A. Burgett, J. Chrom. Sci., 11, 611 (1973).

35. P. Jacquelot and G. Thomas, Bull. Soc. Chim. France, 702 (1971).

36. R.F. Sieck, J.J. Richards, K. Iverson and C.V. Banks, Anal.Chem., 43, 913 (1971).

37. J.W. Mitchell and C.V. Banks, Anal. Chim. Acta, 57, 415 (1971).

38. Y.S. Drug, G.V. Muravieva, K.M. Grinberg and G.N. Niestievenko, Zavodsk. Lab., 38, 1305 (1972).

39. W.D. Ross, Anal. Chem., 35, 1596 (1963).

40. W.D. Ross, R.E. Sievers and G. Wheeler Jr., Anal. Chem., 37, 598 (1965).

41. W.D. Ross and G. Wheeler Jr., Anal. Chem., 36, 266 (1964).

42. P.C. Uden and C.R. Jenkins, Talanta, 16, 892 (1969).

43. H. Veening and J.F.K. Huber, J. Gas Chromatog., 6, 326 (1968).

44. C.A. Burgett and J.S. Fritz, J. Chromatog., 77, 265 (1973).

45. R. Belcher, J.P. Majer, R. Perry and W.I. Stephen, Anal. Chim. Acta, 45, 305 (1969).

46. R. Belcher, J. Majer, R. Perry and W.I. Stephen, J. Inorg. Nucl. Chem., 31, 471 (1969).

47. K. Arakawa and K. Tanikawa, Bunseki Kagaku, 16, 812 (1967).

48. R.E. Sievers, J.W. Connolly, W.D. Ross, J. Gas Chromatog., 5, 241 (1967).

49. K. Tanikawa, H. Ochi and K. Arakawa, Binseki Kagaku, 19, 1669 (1970).

50. J.E. Schwarberg, R.E. Sievers and R.W. Moshier, Anal. Chem., 42, 1828 (1970).

51. R.E. Sievers, J.E. Schwarberg, 158th ACS Meeting, Paper 57, Sept. 1969.

52. R. Belcher, J.P. Majer, R. Perry and W.I. Stephen, Anal. Chim. Acta., 43, 451 (1968).

53. R.E. Sievers, K.J. Eisentraut, C.S. Springer Jr. and D.W. Meek, 152nd ACS Meeting, Paper 66, Sept. 1966.

54. K. Yamakawa, K. Tanikawa and K. Arakawa, Chem. Pharm. Bull., 11, 1405 (1963).

55. A. Kito, Y. Miyabe, H. Kubayashi and K. Ueno, Bunseki Kagaku, 20, 1363 (1971).

56. T. Shigematsu, M. Matsui and K. Utsunomiya, Bull. Inst. Chem. Res., 46, (6), 256 (1968).

57. K. Tanikawa, K. Hirano and K. Arakawa, Chem. Pharm. Bull., 15, 915 (1967).

58. P. Jacquelot and G. Thomas, J. Chromatog, 66, 121 (1972).

59. K.J. Eisentraut, D.G. Johnson, M.F. Richardson and R.E. Sievers, 161st ACS Meeting, Los Angeles, March 1971, Abstract Anal. 90.

60. T. Fuginaga and Y. Ogino, Bull. Chrom. Soc. Japan, 40, 434 (1967).

61. W.D. Ross and R.E. Sievers, Paper 18, 16th Int. Symposium on G.C. and Assoc. Techniques, Rome, Italy, Sept. 20, 1966.

62. W.D. Ross and R.E. Sievers in "Gas Chromatography", A.B. Littlewood, ed., London, England, Elsevier, Elsevier Pub. Co., 1967, pp. 272-282.

63. W.D. Ross and R.E. Sievers, Talanta, 15, 87 (1968).

64. R.E. Sievers, G. Wheeler Jr., and W.D. Ross Jr., J. Gas Chromatog., 4,112 (1966).

65. M.H. Noweir and J. Cholak, Environ. Sci. Technol., 3, 927 (1969).

66. R.T. Ross and M.T. Shafik, 161st ACS Meeting, Los Angeles, March 1971 Abstract Pest. Chem., 80.

67. W.D. Ross and R.E. Sievers, Eviron. Sci. Technol., 6, 1955 (1972).

68. G.M. Frame, R.E. Ford, W.G. Scribner and T. Curtnicek, Anal. Chem., 46, 534 (1974).

69. M.L. Taylor and E.L. Arnold., Anal. Chem., 43, 1328 (1971).

70. M.L. Taylor, E.L. Arnold and R.E. Sievers, Anal. Lett., 1, 735 (1968).

71. J.K. Foreman, T.A. Gough and E.A. Walker, Analyst, 95, 797 (1970).

72. K.J. Eisentraut, D.J. Griest and R.E. Sievers, Anal. Chem., 43, 2003 (1971).

73. W.R. Wolf and R.E. Sievers, 161st ACS Meeting, Los Angeles, March 1971, Abst. Anal. 89.

74. H. Kawaguchi, T. Sakamoto, Y. Yoshida and A. Mizuike, Bunseki Kagaku, 22, 1434 (1973).

75. R. Belcher, J.R. Majer, W.I. Stephen, I.J. Thomson and P.C. Uden, Anal. Chim. Acta, 50, 423 (1970).

76. G.P. Morie, Dissertion Abstr., 27, 1966.

77. G.P. Morie and T.R. Sweet, Anal. Chem., 37, 1552 (1965).

78. J.E. Schwarberg, D.R. Gere and R.E. Sievers, Inorg. Chem., 6, 1933 (1967).

79. J.E. Schwargerg, R.W. Moshier and J.G. Walsh, Talanta, 11, 1213 (1964).

80. R.E. Sievers, K.J. Eisentraut, C.S. Springer Jr., and D.W. Meek, Advances in Chemistry, 71, 141 (1967).

81. K. Utsunomiya, Bull. Chem. Soc. Jap., 44, 2688 (1971).

82. W.C. Butts, Dissert. Abstr., 29, 506-B (1968).

83. T. Dono, Y. Ishikara, K. Sato and T. Nakazawa, Bunseki Kagaku, 15, 181 (1966).

84. T. Fuginaga, T. Kuwamato and S. Murat, Talanta, 18, 429 (1971).

85. K.K. Albert, Anal. Chem., 36, 2034 (1964).

86. V.I. Mishin and S.L. Dodychin, Zh. Priklad. Khim., 43, 1584 (1970).

87. F.M. Zado and R.S. Juvet, Anal. Chem., 38, 569 (1966).

88. G.P. Morie and T.R. Sweet, Anal. Chim. Acta, 34, 314 (1966).

89. R.W. Moshier and D.R. Gere, 151st ACS Meeting, Jan. 1966.

90. C. Genty, C. Howin, P. Mulherbe and R. Schott, Anal. Chem., 43, 235 (1971).

91. C. Genty, C. Howin and R. Schott in "Gas Chromatography 1968", C.L.A., ed., London, England, Elsevier Publishing Co., 1969, pp. 141-157.

92. M. Miyazaki and H. Kaneko, Chem. Pharm. Bull., 18, 1933 (1970).

93. J.R. Stokley, Dissertation Abstract, 27, 1388-B (1966).

94. P. Jacquelot and G. Thomas, Bull. Soc. Chim. France, 3167 (1970).

95. P. Jacquelot and G. Thomas, Compt. Rend. Acad. Sci., 272, 448 (1972).

96. J.E. Tackett, Dissertation Abstract, 26, 3011 (1965).

97. R. Belcher, C.R. Jenkins, W.I. Stephen and P.C. Uden, Talanta, 17, 455 (1970).

98. S.P. Cram and T.R. Booker, Paper 44, 159th ACS Meeting, Feb. 23, 1970.

99. G.H. Booth and W.J. Darby, Anal. Chem., 43, 831 (1971).

100. C.A. Burgett, Hewlett-Packard Applications Note ANC 32-72, 1972.

101. C.A. Burgett and W.J. Campbell, Hewlett-Packard Applications Note GC-74.

102. L.F. Druding and G.B. Kauffman, Coord. Chem., Rev. 3, 409 (1968).

103. L.C. Hansen, W.G. Scribner, T.W. Gilbert and R.E. Sievers, Anal. Chem., 43, 349 (1971).

104. R.S. Juvet and R.P. Durbin, J. Gas Chrom., 1, 14 (1963).

105. R.S. Juvet and R.P. Durbin, Anal. Chem., 38, 565 (1966).

106. R.T. Ross and M.T. Shafik, J. Chrom. Sci., 11, 46 (1973).

107. W.D. Ross, Aerospace Res. Labs. Report ARL 68-0212 (1968).

108. J. Savory, M.T. Glenn and J.A. Ahlstrom, J. Chromatog. Sci., 10, 247 (1972).

109. J. Savory, P. Mushak and F.W. Sunderman Jr., J. Chromatog. Sci., 7, 674 (1969).

110. J. Savory, P. Mushak and F.W. Sunderman Jr., 21st Monthly Mtg., Am. Assoc. Clin. Chem., Aug. 1969, Paper 59.

111. J. Savory, P. Mushak, and F.W. Sunderman Jr., Advan. Chromatog., 181 (1969).

112. J. Savory, P. Mushak, .F.W. Sunderman Jr., R.H. Estes and N.D. Raszel, Anal. Chem., 42, 294 (1970).

113. W.R. Wolf, M.L. Taylor, B.M. Hughes, T.O. Teiran and R.E. Sievers, Anal. Chem., 44, 616 (1972).

114. B.B. Tomazic and J.W. O'Laughlin, Anal. Chem., 45, 1519 (1973).

115. R.E. Sievers, W. Ross, R.W. Moshier and M.L. Morris, Inorg. Chem., 1, 966 (1962).

116. R.W. Moshier and J.E. Schuarberg, Talanta, 13, 445 (1966).

117. W.D. Reynolds, Dissertaion Abstract., 26, (1965).

118. R.F. Sieck and C.U. Banks, Anal. Chem., 44, 2307 (1972).

119. W.D. Ross, W.G. Scribner and R.E. Sievers in "Gas Chromatography 1970", R. Stock, ed., London, England, Elsevier Pub. Co., 1971, pp. 369-380.

120. H. Veening, W. Bachman and D.M. Wilkinson, J. Gas Chromatog., 5, 248 (1967).

121. E. Bayer and H.P. Muller, Tetrahedron Lett., 6, 533 (1971).

122. E. Bayer, H.P. Muller and R.E. Sievers, Anal. Chem., 43, 2012 (1971).

123. R. Belcher, W.I. Stephen, I.J. Thomson and P.C. Uden, J. Inorg. Nucl. Chem., 33, 1851 (1971).

124. R.S. Barratt, Proc. Soc. Anal. Chem., 9, 86 (1972).

125. R.S. Barratt, R. Belcher, W.I. Stephen and P.C. Uden, Anal. Chim. Acta, 59, 59 (1972).

126. R. Belcher, R. Martin, W.F. Stephen, D.E. Henderson, H. Kamalizad and P.C. Uden, Anal. Chem., 47, 1197 (1973).

127. R. Belcher, W.I. Stephen, IlJ. Thomson and P.C. Uden , Chem. Commun., 16, (1970).

128. R. Belcher, W.I. Stephen, I.J. Thomson and P.C. Uden, J. Inorg. Nucl. Chem., 34, 1017 (1972).

129. W.I. Stephen, I.J. Thomson and P.C. Uden, Chem. Commun., 269 (1969).

130. R. Belcher, M. Pravica, W.I. Stephen and P.C. Uden, Chem. Commun., 41, (1971).

131. R. Belcher, K. Blessel, T. Cardwell, M. Pravica, W.I. Stephen and P.C. Uden, J. Inorg. Nucl. Chem., 35, 1127 (1973).

132. P.C. Uden, R. Belcher, M. Pravica, W.I. Stephen, J. Chrom. Soc., 1, 41 (1971).

133. P.C. Uden, D.E. Henderson and C.A. Burgett., Anal. Letters, Dec. 1974.

134. P.C. Uden, K. Blessel and D. Henderson, 163rd ACS Meeting, Boston, April 10, 1972, Abst. Anal. 36.

135. P.C. Uden and K. Blessel, Inorg. Chem., 12, 352 (1973).

136. M. Miyazaki, T. Imanari, T. Kanugi and Z. Tamara, Chem. Pharm. Bull., 14, 117 (1966).

137. M. Miyazaki, T. Imanari, T. Kunugi and Z. Tamara, Chem. Pharm. Bull., 14, 117 (1966).

138. M.F. Richardson and R.E. Sievers, J. Inorg. Nucl. Chem., 32, 1895 (1970).

139. T. Fuginaga, T. Kuwamato and Y. Ono, Bunseki Kugaku, 12, 1199 (1963).

140. T. Fuginaga, T. Kuwamato and Y. Ono, J. Chem. Soc. Japan, 86, 1294 (1965).

141. R.E. Sievers, J.W. Connolly and W.D. Ross in "Advances in Gas Chromatography 1967", A. Zlatkis, ed., Evanston, Ill., Preston Technical Abstracts Co., 1967, pp. 104-10.

142. R.J. Majer, Science Tools, 15, 11 (1968).

143. R.W. Moshier and D.R. Gere, 152nd ACS Meeting, Sept. 1966.

144. M.F. Richardson and R.E. Sievers, Inorg. Chem., 10, 498 (1971).

145. T. Shigematsu, M. Matsui and K. Utsunomyia, Bull. Chem. Soc. Japan, 41, 763 (1968).

146. T. Shigematsu, M. Matsui and K. Utsunomiya, Bull. Chem. Soc. Japan, 42, 1278 (1969).

147. M. Tanka, T. Shono and K. Shinra, Anal. Chim. Acta, 43, 157 (1968).

148. K. Utsunomiya, Anal. Chim. Acta, 59, 147 (1972).

149. K. Utsunomiya and T. Shigematsu, Bull. Chem. Soc. Japan, 45, 303 (1972).

150. R. Fontaine, B. Santoni, C. Pommier and G. Guiochon, Chromatographia, 3, 532 (1970).

151. R.D. Hill and H.J. Gesser, J. Gas Chromatog., 1, 11 (1963).

152. R. McCoy, Dissertation Abstr., 33, (1970).

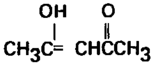
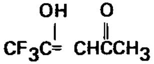
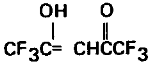
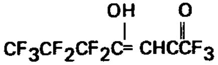
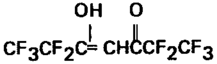
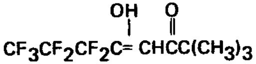
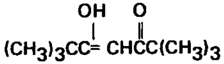
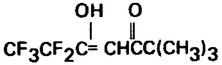
153. W.D. Ross, Proc. Univ. Mo. Ana. Conf., 279 (1968).

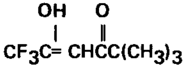
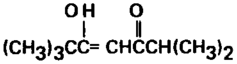
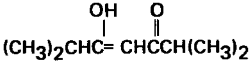
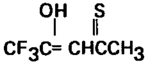
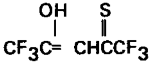
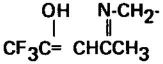
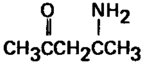
154. W.D. Ross and R.E. Sievers in "Development in Applied Spectroscopy", Vol. 8, New York, New York, Plenum Press, 1970, pp. 181-92.

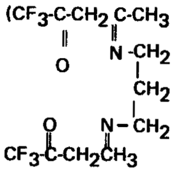
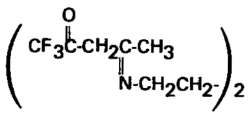
155. R.E. Sievers, G. Wheeler Jr. and W.D. Ross in "Advances in Gas Chromatography", H. Zlatkis and L.S. Ettre, eds., Evanston, Ill. Preston Technical Abstracts Co., 1966, p. 112.

156. J. Warren and A.G. Smeeth, Proc. Soc. Anal. Chem., 9, 194 (1972).

APPENDIX

NAME	ABBREVIATION	STRUCTURE
2,4-pentanedione	H(ACAC)	 $CH_3\overset{\overset{OH}{\vert}}{C}{=}\ CH\overset{\overset{O}{\Vert}}{C}CH_3$
1,1,1-trifluoro-2,4-pentanedione	H(TFA)	 $CF_3\overset{\overset{OH}{\vert}}{C}{=}\ CH\overset{\overset{O}{\Vert}}{C}CH_3$
1,1,1,5,5,5-hexafluoro-2,4-pentanedione	H(HFA)	 $CF_3\overset{\overset{OH}{\vert}}{C}{=}\ CH\overset{\overset{O}{\Vert}}{C}CF_3$
1,1,1,2,2,3,3,7,7,7-decafluoro-4,6-heptanedione	H(DFHD)	 $CF_3CF_2CF_2\overset{\overset{OH}{\vert}}{C}{=}\ CH\overset{\overset{O}{\Vert}}{C}CF_3$
1,1,1,2,2,6,6,7,7,-decafluoro-3,5-heptanedione	H(FHD)	 $CF_3CF_2\overset{\overset{OH}{\vert}}{C}{=}\ CH\overset{\overset{O}{\Vert}}{C}CF_2CF_3$
1,1,1,2,2,3,3.-heptafluoro-7,7-dimethyl-4,6,-octanedione	H(FOD)	 $CF_3CF_2CF_2\overset{\overset{OH}{\vert}}{C}{=}\ CH\overset{\overset{O}{\Vert}}{C}C(CH_3)_3$
2,2,6,6-tetramethyl-3,5-heptanedione	H(THD)	 $(CH_3)_3C\overset{\overset{OH}{\vert}}{C}{=}\ CH\overset{\overset{O}{\Vert}}{C}C(CH_3)_3$
1,1,1,2,2-pentanedionedimethyl-3,5-heptanedione	H(PHD)	 $CF_3CF_2\overset{\overset{OH}{\vert}}{C}{=}\ CH\overset{\overset{O}{\Vert}}{C}C(CH_3)_3$

1,1,1-trifluoro-6, 6-dimethyl-2,4-heptanedione	H(PTA)	 $CF_3\overset{\overset{OH}{\mid}}{C}=CH\overset{\overset{O}{\|}}{C}C(CH_3)_3$
2,2,6-trimethyl-3,5-heptanedione	IBPM	 $(CH_3)_3C\overset{\overset{OH}{\mid}}{C}=CH\overset{\overset{O}{\|}}{C}CH(CH_3)_2$
2,6-dimethyl-3,5-heptanedione	H(DMH)	 $(CH_3)_2CH\overset{\overset{OH}{\mid}}{C}=CH\overset{\overset{O}{\|}}{C}CH(CH_3)_2$
1,1,1-trifluoro-2-hydroxylpent-2-en-4-thione	H(T-TFA)	 $CF_3\overset{\overset{OH}{\mid}}{C}=CH\overset{\overset{S}{\|}}{C}CH_3$
1,1,1,5,5,5-hexafluoro-2-hydroxylpent-2-en-4-thione	H(T-HFA)	 $CF_3\overset{\overset{OH}{\mid}}{C}=CH\overset{\overset{S}{\|}}{C}CF_3$
bis-trifluoroacetylacetone-ethylenedi-imine	$H_2(enTFA_2)$	 $CF_3\overset{\overset{OH}{\mid}}{C}=CH\overset{\overset{N\text{-}CH_2\text{-}}{\|}}{C}CH_3$
4-aminopent-3-en-2-one	AMO	 $CH_3\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{NH_2}{\mid}}{C}CH_3$
Tri-n-butylphosphate	TBP	$(C_4H_9O)_3\text{-}P\rightarrow O$
Di-n-butylsulfoxide	DBSO	$(C_4H_9)_2\text{-}S\rightarrow O$

NAME	ABBREVIATION	STRUCTURE
Bis-trifluoroacetylacetone propylenedi-imine	$H_2(pn\ TFA)_2$	
Bis-trifluoroacetylacetone butylenedi-imine	$H_2\ (buTFA)_2$	

1. Albert, K.K., Anal. Chem. 36, 2034 (1964).
2. Anvaer, B.I. and Drugov, Y.S., Zh. Anal. Khim. 26, 1180 (1971).
3. Arakawa, K. and Tanikawa, K., Bunseki Kagaku 15, 398 (1966).
4. Arakawa, K. and Tanikawa, K., Bunseki Kagaku 16, 812 (1967).
5. Barratt, R.S., Proc. Soc. Anal. Chem. 9, 86 (1972).
6. Barratt, R.S., Proc. Soc. Anal. Chem. 10, 167 (1973).
7. Barratt, R.S., Belcher, R., Stephen, W.I. and Uden, P.C., Anal. Chim. Acta 59, 59 (1972).
8. Bayer, E. and Muller, H.P., Tetrahedron Lett. 6, 533 (1971).
9. Bayer, E., Muller, H.P. and Sievers, R. E., Anal. Chem. 43, 2012 (1971).
10. Belcher, R., Blessel, K., Cardwell, T. Pravica, M., Stephen, W.I. and Uden, P.C., J. Inorg. Nucl. Chem. 35, 1127 (1973).
11. Belcher, R., Jenkins, C.R., Stephen, W.I. and Uden, P.C., Talanta 17, 455 (1970).
12. Belcher, R., Majer, J.P., Perry, R. and Stephen, W.I., Anal. Chim. Acta 43, 451 (1968).
13. Belcher, R., Majer, J.P., Perry, R. and Stephen, W.I., Anal. Chim. Acta 45, 305 (1969).
14. Belcher, R., Majer, J., Perry, R. and Stephen, W.I., J. Inorg. Nucl. Chem. 31, 471 (1969).
15. Belcher, R., Majer, J.R., Stephen, W.I., Thomson, I.J. and Uden, P.C., Anal, Chim. Acta 50, 423 (1970).
16. Belcher, R., Martin, R., Stephen W.F., Henderson, D.E., Kamalizad, H. and Uden, P.C., Anal. Chem. 47, 1197 (1973).
17. Belcher, R., Pravica, M., Stephen, W.I. and Uden, P.C., Chem. Commun. 41 (1971).
18. Belcher, R., Stephen, W.I., Thomson, I.J. and Uden, P.C., J. Inorg. Nucl. Chem. 33, 1851 (1971).
19. Belcher, R., Stephen, W.I., Thomson, I.J. and Uden, P.C., Chem. Commun. 16 (1970).
20. Belcher, R., Stephen, W.I., Thomson, I.J., and Uden, P.C., J. Inorg. Nucl. Chem. 34, 1017 (1972).
21. Biermann, W.J., and Gesser, H., Anal. Chem. 32, 1525 (1960).
22. Booth, G.H. and Darby, W.J., Anal. Chem. 43, 831 (1971).
23. Burgett, C.A., Ph.D Thesis, Ames, Iowa, Library, Iowa State University, 1972.
24. Burgett, C.A., Hewlett-Packard Applications Note ANC 32-72, 1972.
25. Burgett, C.A., Presented at Midatlantic Regional ACS Meeting, Jan 14, 1973.
26. Burgett, C.A., Paper 87, 24th Pittsburgh Conference, March 6, 1973.
27. Burgett, C.A., J. Chrom. Sci. 11, 611 (1973).
28. Burgett, C.A. and Campbell, W.J., Hewlett-Packard Applications Note GC-7-74.
29. Burgett, C.A. and Fritz, J.S., Anal. Chem. 44, 1738 (1972).
30. Burgett, C.A. and Fritz, J.S., Talanta 20, 363 (1973).
31. Burgett, C.A. and Fritz, J.S., J. Chromatog. 77, 265 (1973).

32. Butts, W.C., Dissert, Abstr., 29, 506—B (1968).
33. Butts, W.C. and Banks, C.V., Anal. Chem. 42, 133 (1970).
34. Carey, M.A., Ph.D. Thesis, Ames, Iowa, Library, Iowa State University, 1967.
35. Cram, S.P. and Booker, T.R., Paper 44, 159th ACS Meeting, Feb. 23, 1970.
36. Dono, T., Ishikara, Y., Sato, K. and Nakazawa, T., Bunseki Kagaku, 15, 181 (1966).
37. Druding, L.F. and Kauffman, G.B., Coord. Chem. Rev. 3, 409 (1968).
38. Drug Y.S., Muravieva, G.V., Grinberg, K.M. and Niestievenko, G.N., Zavodsk. Lab. 38, 1305 (1972).
39. Duswalt, A.A., Disser. Abstr., 20, 52 (1959).
40. Eisentraut, K.J., Griest, D.J., and Sievers, R.E., Anal. Chem. 43, 2003 (1971).
41. Eisentraut, K.J., Johnson, D.G., Richardson, M.F., and Sievers, R.E. 161st ACS Meeting, Los Angeles, March, 1971, Abstract Anal. 90.
42. Eisentraut, K.J. and Sievers, R.E., Amer. Chem. Soc. 87, 5254 (1965).
43. Eisentraut, K.J. and Sievers, R.E., 19th ACS Summer Symposium, Edmonton, Conn., June 22, 1966.
44. Eisentraut, K.J. and Sievers, R.E., U.S. Patent 3,429,904, Feb. 25, 1969.
45. Eisentraut, K.J. and Sievers, R.E., U.S. Patent 3,453,319, July 1, 1969.
46. Fernando, Q., Frieser, H. and Wise, E., Anal. Chem. 35, 1994 (1963).
47. Ferraro, J.R. and Healy, T.V., J. Inorg, Nucl. Chem. 24, 1463 (1962).
48. Fontaine, R., Santoni, B., Pommier, C., and Guiochon, G., Chromatographia 3, 532 (1970).
49. Foreman, J.K., Gough, T.A., and Walker, E.A., Analyst 95, 797 (1970).
50. Frame, G.M., Ford, R.E. Scribner, W.G., and Curtnicek, T., Anal. Chem., 46 (1974).
51. Fuginaga, T., Kuwamato, T., and Ono, Y., Bunseki Kugaku, 12, 1199 (1963).
52. Fuginaga, T., Kuwamato, T., and Ono, Y., J. Chem. Soc. Japan, 86, 1294 (1965).
53. Fuginaga, T., Kuwamato, T., and Murat, S., Talanta 18, 429 (1971).
54. Fuginaga, T., and Ogino, Y., Bull. Chrom. Soc. Japan, 40, 434 (1967).
55. Genty, C., Howin, C., Mulherbe, P. and Schott, R., Anal. Chem. 43, 235 (1971).
56. Genty, C., Howin, C. and Schott, R., in " Gas Chromatography 1968," C.L.A., Ed., London, England, Elsevier Publishing Co., 1969, pp. 141-157.
57. Guiochon, G. and Pommier, C., "Gas Chromatography in Inorganic and Organometallics," Ann Arbor Science Publisher, Inc., Ann Arbor, MI, 1973.
58. Hansen, L.C., Scribner, W.G., Gilbert, T.W. and Sievers, R.E., Anal. Chem. 43, 349 (1971).
59. Hazeldine, R.N., Musgrave, W.K.R., Smith, F. and Turton, L.M., J. Chem. Soc. 609 (1951).
60. Hill, R.D. and Gesser, H., J. Gas Chromatog. 1, 11 (1963).
61. Jacquelot, P. and Thomas, G., Bull, Soc. Chim, France, 3167 (1970).
62. Jacquelot, P. and Thomas, G., Bull. Soc. Chim, France, 702 (1971).

63. Jacquelot, P. and Thomas, G., Compt. Rend. Acad. Sci., 272, 448 (1972).
64. Jacquelot, P. and Thomas, G., J. Chromatog, 66, 121 (1972).
65. Jacquelot, P. and Thomas, G., Bull. Soc. Chim. France, 1261 (1973).
66. James, A.T. and Martin, A.J.P., Biochem. J. Proc. 48, 7 (1951).
67. James, A.T. and Martin, A.J.P., Analyst 77, 915 (1952).
68. Juvet, R.S. and Durbin, R.P., J. Gas Chrom., 1, 14 (1963).
69. Juvet, R.S. and Durbin, R.P., Anal. Chem. 38, 565 (1966).
70. Kawaguchi, H., Sakamoto, T., Yoshida, Y., and Mizuike, A., Bunseki Kagaku 22, 1434 (1973).
71. Kito, A., Miyabe, Y., Kubayashi, H. and Ueno, K., Bunseki Kagaku, 20, 1363 (1971).
72. Kuwamoto, T., Bunseki Kagaku, 21, 445 (1972).
73. Lederer, M., Nature 176, 462 (1955).
74. Majer, R.J., Science Tools 15, 11 (1968).
75. McCoy R., Dissertation Abstr., 33 (1970).
76. Mishin, V.I. and Dodychin, S.L., Zh. Priklad. Khim., 43, 1584 (1970).
77. Mitchell, J.W., Ph.D. Thesis, Ames, Iowa, Library, Iowa State University, 1970.
78. Mitchell, J.W. and Banks, C.V., Anal. Chim. Acta 57, 415 (1971).
79. Miyazaki, M. and Kaneko, H., Chem. Pharm. Bull., 18, 1933 (1970).
80. Miyazaki, M., Imanari, T., Kanugi, T. and Tamara, Z., Chem. Pharm. Bull., 14, 117 (1966).
81. Morgan, G.T. and Moss, H.W., J. Chem. Soc. 105, 189 (1914).
82. Morie, G.P., Dissertion Abstr., 27, 1966.
83. Morie, G.P. and Sweet, T.R., Anal. Chem. 37, 1552 (1965).
84. Morie, G.P. and Sweet, T.R., Anal. Chim. Acta 34, 314 (1966).
85. Morris, N.L., Moshier, R.W. and Sievers, R.E., Inorg Chem. 2, 411 (1963).
86. Moshier, R.W. and Gere, D.R., 152nd ACS Meeting, Sept. 1966.
87. Moshier, R.W. and Gere, D.R., 151st ACS Meeting, Jan. 1966.
88. Moshier, R.W. and Schearberg, J.E., Talanta 13, 445 (1966).
89. Moshier, R.W. and Sievers, R.E., " Gas Chromatography of Metal Chelates," New York, Pergamon Press, Inc., 1965.
90. Myazki, M., Imanari, T., Kunugi, T., and Tamura, Z., Chem. Pharm. Bull., 14, 117 (1966).
91. Noweir, M.H. and Cholak, J., Environ, Sci. Technol. 3, 927 (1969).
92. Pommier, C., Revue de Chimie Minerale 3, 401 (1966).
93. Reynolds, W.D., Dissertation Abstract., 26, 1965.
94. Richardson, M.F. and Sievers, R.E., J. Inorg. Nucl. Chem., 32, 1895 (1970).
95. Richardson, M.F. and Sievers, R.E., Inorg. Chem. 10, 498 (1971).
96. Ross, R.T. and Shafik, M.T., 161st ACS Meeting, Los Angeles, March 1971, Abstract Pest. Chem. 80.
97. Ross, R.T., and Shafik, M.T., J. Chrom. Sci. 11, 46 (1973).

98. Ross, W.D., Anal. Chem. 35, 1596 (1963).
99. Ross, W.D., Proc. Univ. Mo. Anna. Conf., 279 (1968).
100. Ross, W.D., Aerospace Res. Labs. Report ARL 68-0212 (1968).
101. Ross, W.D., Scribner, W.G. and Sievers, R.E., in "Gas Chromatography 1970," Stock, R., Ed., London, England, Elsevier Publishing Co., 1971, pp. 369-380.
102. Ross, W.D., and Sievers, R.E., Paper 18, 16th Int. Symposium on G.C. and Assoc. Techniques, Rome, Italy, Sept. 20, 1966.
103. Ross, W.D. and Sievers, R.E., in "Gas Chromatography," Littlewood, A.B., Ed., London, England, Elsevier, Elsevier Publishing Co., 1967, pp. 272-282.
104. Ross, W.D. and Sievers, R.E., Talanta 15, 87 (1968).
105. Ross, W.D. and Sievers, R.E., Anal. Chem. 41, 1109 (1969).
106. Ross, W.D. and Sievers, R.E., in "Development in Applied Spectroscopy," Vol. 8, New York, New York, Plenum Press, 1970, pp. 181-92.
107. Ross, W.D. and Sievers, R.E., Environ, Sci. Technol. 6, 155 (1972).
108. Ross, W.D., Sievers, R.E. and Wheeler, G., Jr., Anal. Chem. 37, 598 (1965).
109. Ross, W.D. and Wheeler, G., Jr., Anal. Chem. 36, 266 (1964).
110. Savory, J., Glenn, M.T. and Ahlstrom, J.A., J. Chromatog. Sci. 10, 247 (1972).
111. Savory, J., Mushak, P. and Sunderman, F.W., Jr., J. Chromatog. Sci. 7, 674 (1969),
112. Savory, J., Mushak, P. and Sunderman, F.W., Jr., 21st. Moth. Mtg., Am. Assoc. Clin. Chemistry, Aug. 1969, paper 59.
113. Savory, J., Mushak, P., Sunderman, F.W., Jr., Advan. Chromatog., 181 (1969).
114. Savory, J., Mushak, P., Sunderman, F.W., Jr., Estes, R.H. and Raszel, N.D., Anal. Chem. 42, 294 (1970).
115. Schwarberg, J.E., Gere, D.R. and Sievers, R.E., Inorg. Chem. 6, 1933 (1967).
116. Schwarberg, J.E., Moshier, R.W., and Walsh, J.G., Talanta, 11, 1213 (1964).
117. Schwarberg, J.E., Sievers, R.E., and Moshier, R.W., Anal. Chem. 42, 1828 (1970).
118. Shigematsu, T., Matsui, M. and Utsunomyia, K., Bull. Chem. Soc. Japan. 41, 763 (1968).
119. Shigematsu, T., Matsui, M. and Utsunomiya, K., Bull. Inst. Chem. Res. 46, (6), 256 (1968).
120. Shigematsu, T., Matsui, M. and Utsunomiya, K., Bull. Chem. Soc. Japan 42, 1278 (1969).
121. Sieck, R.F., Ph.D. Thesis, Ames, Iowa, Library, Iowa State University, 1971.
122. Sieck, R.F. and Banks, C.U., Anal. Chem. 44, 2307 (1972).
123. Sieck, R.F., Richards, J.J., Iverson, K. and Banks, C.V., Anal Chem. 43, 913 (1971).
124. Sievers, R.E., in "Coordination Chemistry, Proceedings John C. Bailor Jr. Symposium," Kirschner, S., Ed., New York, New York, Plenum Press, 1969, pp. 270-88.
125. Sievers, R.E., Connolly, J.W. and Ross, W.D., J. Gas Chromatog. 5, 241 (1967).

126. Sievers, R.E., Connolly, J.W. and Ross, W.D., in "Advances in Gas Chromatography 1967," Zlatkis, A., Ed., Evanston, Ill., Preston Technical Abstracts Co., 1967, pp. 104-10.
127. Sievers, R.E., Eisentraut, K.J., Springer, C.S., Jr., and Meek, D.W., 152nd ACS Meeting, paper 66, Sept. 1966.
128. Sievers, R.E., Eisentraut, K.J., Springer, C.S., Jr., and Meek, D.W., Advances in Chemistry, 71, 141 (1967).
129. Sievers, R.E., Ponder, B.W., Morrie, M.L. and Moshier, R.W., Inorg. Chem. 2, 693 (1963).
130. Sievers, R.E., Ross, W., Moshier, R.W. and Morris, M.L., Inorg. Chem. 1, 966 (1962).
131. Sievers, R.E., Schwarberg, J.E., 158th ACS Meeting, paper 57, Sept. 1969.
132. Sievers, R.E., Wheeler, G., Jr., and Ross, W.D., in "Advances in Gas Chromatography," Zlatkis, H. and Ettre, L.S., Eds., Evanston, Ill., Preston Technical Abstracts Co., 1966 p. 112.
133. Sievers, R.E., Wheeler, G., Jr., and Ross, W.D., J. Gas Chromatog. 4, 112 (1966).
134. Sokolov, D.N., Zh Analit. Kim. 27, 993 (1972).
135. Springer, C.D., Jr., Meek, D.W. and Sievers, R.E., Inorg. Chem. 6, 1105 (1967).
136. Stephen, W.I., Proc. Soc. Anal. Chem, 9, 137 (1972).
137. Stephen, W.I., Thomson, I.J. and Uden, P.C., Chem. Commun. 269 (1969).
138. Stokley, J.R., Dissertation Abstract, 27, 1388-B (1966).
139. Sweet, T.R. and Parlett, H.W., Anal. Chem. 40, 1885 (1968).
140. Tackett, J.E., Dissertation Abstract, 26, 3011 (1965).
141. Tanka, M., Shono, T. and Shinra, K., Anal. Chim. Acta 43, 157 (1968).
142. Tanikawa, K., Ochi, H. and Arakawa, K., Binseki Kagaku 19, 1669 (1970).
143. Tanikawa, K., Hirano, K. and Arakawa, K., Chem. Pharm. Bull. 15, 915 (1967).
144. Taylor, M.L. and Arnold, E.L., Anal. Chem. 43, 1328 (1971).
145. Taylor, M.L., Arnold, E.L. and Sievers, R.E., Anal. Lett. 1, 735 (1968).
146. Tomazic, B.B. and O'laughlin, J.W., Anal. Chem., 45, 1519 (1973).
147. Uden, P.C., Belcher, R., Pravica, M., Stephen, W.I., J. Chrom. Soc. 1, 41 (1971).
148. Uden, P.C., Henderson, D.E., and Burgett, C.A., Anal. Letters, Dec. 1974.
149. Uden, P.C., Blessel, K. and Henderson, D., 163rd ACS, Meeting, Boston, April 10, 1972, Abst. Anal. 36.
150. Uden, P.C., and Blessel, K., Inorg, Chem. 12, 352 (1973).
151. Uden, P.C. and Jenkins, C.R., Talanta, 16, 892 (1969).
152. Utsunomiya, K., Bull. Chem. Soc. Jap. 44, 2688 (1971).
153. Utsunomiya, K., Anal. Chim. Acta 59, 147 (1972).
154. Utsunomiay, K., and Shigematsu, T., Bull. Chem. Soc. Jap., 45, 303 (1972).
155. Utsunomiya, K. and Shigematsu, T., Anal. Chim. Acta, 58, 411 (1972).
156. Veening, H., Bachman, W. and Wilkinson, D.M., J. Gas Chromatog., 5, 248 (1967).
157. Veening, H. and Huber, J.F.K., J. Gas Chromatog, 6, 326 (1968).

158. Warren, J. and Smeeth, A.G., Proc Soc. Anal. Chem. 9, 194 (1972).

159. Wolf, W.R. and Sievers, R.E., 161st A.C.S. Meeting, Los Angeles, March 1971, Abst. Anal. 89.

160. Wolf, W.R., Taylor, M.L., Hughes, B.M., Tieran, T.O. and Sievers, R.E., Anal. Chem. 44, 616 (1972).

161. Yamakawa, K., Tanikawa, K. and Arakawa, K., Chem. Pharm. Bull. 11, 1405 (1963).

162. Zado, F.M. and Juvet, R.S., Anal. Chem. 38, 569 (1966).