

Gas Chromatography of Divalent Transition Metal Chelates

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The thermal and gas chromatographic behavior of volatile metal chelates of four types of ligand, β -diketones, monothio- β -diketones (β -thioketones), bidentate and tetradentate β -ketoamines is compared for Cu(II) and Ni(II), with discussion also of Pd(II) and Pt(II). Relative thermal and chemical stabilities are compared and the potential for quantitative analytical utility of the complexes investigated with regard to gas chromatographic behavior, detection limits, and resolution of different metal chelates. Optimal complex formation conditions are reported. Nickel chelates show somewhat greater stability and lower detection limits than their copper analogs with the exception of the tetradentate β -ketoamine complexes where linear quantitation is straightforward in the microgram to nanogram range and below.

Gas chromatographic analysis of volatile metal chelates is established as a trace method, particularly for β -diketone complexes of trivalent hexacoordinating metal ions (1-3). While the stability of fluorinated β -diketonates of chromium, aluminum, beryllium, and some other metals has allowed quantitative determination to the picogram level employing electron capture detection (4-6) and mass spectrometry (7-9), many metal β -diketonates have chemical properties which make quantitative GC impracticable.

Divalent transition metals in particular form β -diketonates which exhibit ready oxidation, polymerization, or solvation (hydration) (10-11). If the metal has a coordination number greater than four, the neutral chelate molecule may act as a Lewis acid forming stable base adducts, the presence of which precludes ready volatilization (11). Even in the case of copper(II) β -diketonates which are usually monomeric and nonhydrated, gas chromatographic behavior is insufficiently ideal to allow determination below the microgram level. The complexes are subject to

considerable peak tailing even under deactivated column conditions and decomposition at low levels is evident.

The gas chromatography of nickel group β -diketonates has proved particularly difficult. While a few highly fluorinated nickel and palladium chelates have been eluted, their characteristics are still generally unsatisfactory for quantitation (12). Typically the dihydrates of the bis chelates persist in nonaqueous solvents and complicate vaporization even if polymerization is not evident.

Our attention in recent years has been drawn to the potentialities of alternative bidentate and tetradentate ligands containing donor atoms other than oxygen as precursors for the formation of more stable and chemically advantageous chelates of these metals which may prove suitable for gas chromatography.

We have reported on the gas chromatographic characteristics of monothio- β -diketonates (13, 14) (β -thioketonates) of the type exhaustively studied by Livingstone, Uhlemann, and others (15, 16). Fluorinated chelates of this type have given good results for Ni(II), Pd(II), and Pt(II) and in some cases for Co(II) and Zn(II) (14). The application of electron capture gas chromatography to trace metal determination has proved successful down to 5×10^{-11} gram levels, but stabilities of the other metal chelates may prevent quantitation to such levels (17). Bayer *et al.* have also reported the preparation and GC-MS study of Ni(II), Pd(II), and Pt(II) chelates of monothio-hexafluoroacetylacetone to the microgram level (18).

The area of Schiff base complexes, in particular chelates of β -ketoamines (19) is another fruitful field for the application of gas chromatographic analysis to divalent transition metals (20-23). In general, the ligands are readily prepared and purified, quantitative reaction with the d^8 metal ions of the nickel group is readily achieved and the analogous copper(II) complexes are also readily chromatographed. In this paper we present results primarily

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- (1) R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates," Pergamon Press, Oxford, 1965, and references therein.
- (2) W. D. Ross and R. E. Sievers, *Anal. Chem.*, **41**, 1109 (1969).
- (3) J. Savory, P. Mushak, F. W. Sunderman, Jr., R. Estes, and N. Roszel, *Anal. Chem.*, **42**, 294 (1970).
- (4) K. J. Eisentraut, D. J. Griest and R. E. Sievers, *Anal. Chem.*, **43**, 2003 (1971).
- (5) M. H. Noweir and J. Cholak, *Environ. Sci. Technol.*, **3**, 927 (1969).
- (6) J. K. Foreman, T. A. Gough, and E. A. Walker, *Analyst (London)*, **95**, 797 (1970).
- (7) J. L. Booker, T. L. Isenhour, and R. E. Sievers, *Anal. Chem.*, **41**, 1705 (1969).
- (8) N. M. Frew, J. J. Leary and T. L. Isenhour, *Anal. Chem.*, **44**, 665 (1972).
- (9) R. Belcher, J. R. Majer, W. I. Stephen, I. J. Thomson, and P. C. Uden, *Anal. Chim. Acta*, **50**, 423 (1970).
- (10) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966).
- (11) D. F. Graddon, *Coord. Chem. Rev.*, **4**, 1 (1969).

- (12) R. E. Sievers, J. W. Connolly, and W. D. Ross, *J. Gas Chromatogr.*, **5**, 241 (1967).
- (13) R. Belcher, W. I. Stephen, I. J. Thomson, and P. C. Uden, *J. Inorg. Nucl. Chem.*, **33**, 1851 (1971).
- (14) R. Belcher, W. I. Stephen, I. J. Thomson, and P. C. Uden, *J. Inorg. Nucl. Chem.*, **34**, 1017 (1972).
- (15) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Aust. J. Chem.*, **18**, 673 (1965) and subsequent papers.
- (16) E. Uhlemann, G. Klose, and H. Müller, *Z. Naturforsch. B.*, **19**, 952, 962 (1964) and subsequent papers.
- (17) R. S. Barrett, R. Belcher, W. I. Stephen, and P. C. Uden, *Anal. Chim. Acta*, **58**, 107 (1972).
- (18) E. Bayer, H. P. Müller, and R. E. Sievers, *Anal. Chem.*, **43**, 2012 (1971).
- (19) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966).
- (20) M. Miyazaki, T. Imanari, T. Kunugi, and Z. Tamura, *Chem. Pharm. Bull. (Jap.)*, **14**, 117 (1966).
- (21) R. Belcher, M. Pravica, W. I. Stephen, and P. C. Uden, *Chem. Commun.*, **1971** 41.
- (22) R. Belcher, K. Blessel, T. J. Cardwell, M. Pravica, W. I. Stephen, and P. C. Uden, *J. Inorg. Nucl. Chem.*, in press.
- (23) P. C. Uden and K. Blessel, *Inorg. Chem.*, **12**, 352 (1973).

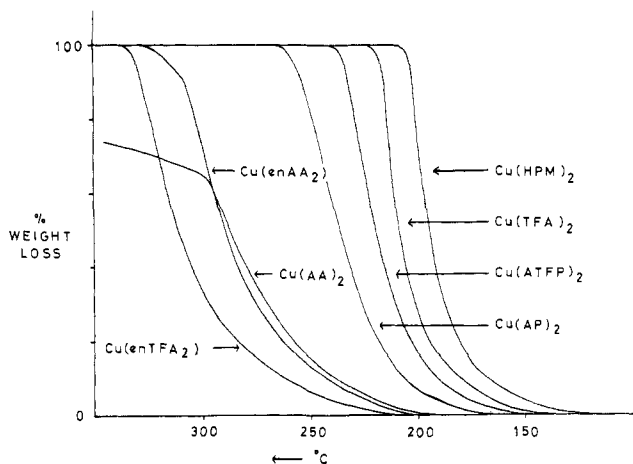


Figure 1. Thermograms of Cu(II) β -diketonates, bidentate and tetradentate β -ketoamine chelates

2-mg samples. Heating rate 5°C min^{-1}

from this group of chelates, making appropriate comparison with the behavior of analogous oxygen and sulfur chelated complexes.

EXPERIMENTAL

General Nomenclature. A general nomenclature of trivial names is used in diagrams and in the text for simpler presentation:

- Pentan-2,4-dione (acetylacetone), H(AA).
- 1,1,1-Trifluoropentan-2,4-dione (trifluoroacetylacetone), H(TFA).
- 1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octanedione (heptafluorobutanoylpivalymethane); H(HPM).
- 2-Mercaptopent-2-en-4-one (monothioacetylacetone); H(T-A).
- 1,1,1-Trifluoro-2-hydroxypent-2-en-4-thione, (monothiotrifluoroacetylacetone); H(T-TFA).
- 4-Aminopent-3-en-2-one; H(AP).
- 4-Amino-1,1,1-trifluoropent-3-en-2-one; H(ATFP).
- N,N'*-ethylenebis(acetylacetoneimine), [bis(acetylacetone)-ethylenediimine]; $\text{H}_2(\text{enAA}_2)$.
- N,N'*-ethylenebis(trifluoroacetylacetoneimine), [bis(trifluoroacetylacetone)ethylenediimine]; $\text{H}_2(\text{enTFA}_2)$.

Preparation of Ligands. β -Ketoamines. In trace gas chromatographic analysis of metal chelates, the removal of higher boiling impurities from the reactant ligand is of prime importance to avoid interference with chelate peaks. Described here are typical procedures for the preparation and purification of two α,β -unsaturated β -ketoamine ligands.

4-Amino-1,1,1-trifluoro-pent-3-en-2-one [(H) ATFP]. A five- to tenfold excess of aqueous ammonia is added to a 10% trifluoroacetylacetone (HTFA) solution in a 3:1, ethanol:chloroform solvent. A one-phase system should just be formed, a little more ethanol being added to ensure this if necessary.

Gas chromatographic analysis shows optimal yields of the β -ketoamine to be obtained by stirring and then allowing the solution to evaporate in an open vessel for 24 hours at ambient temperature. A two-phase system is then formed, the (H)ATFP being recovered in 60–70% yield from the chloroform layer. The aqueous layer contains ammonium trifluoroacetate which is the major by-product, but no (H)ATFP.

Purification of the ligand is best accomplished by vacuum sublimation followed by silica gel column chromatograph (Brockman Grade 2.5) of the sublimate using 1:2 acetone:benzene as eluent. Impurities remain adsorbed and the ligand is eluted in less than 10 minutes from a 2-foot column. *Anal.* Calcd: C, 39.2; H, 3.9; N, 9.2. Found: C 38.7; H, 3.9; N, 9.2.

***N,N'*-ethylenebis(trifluoroacetylacetoneimine); [(bis(trifluoroacetylacetone)-ethylenediimine)], $\text{H}_2(\text{enTFA}_2)$.** Excess ethylenediamine (12 ml) is added to a solution of 40 ml of HTFA in 150 ml of 95% ethanol at 70°C . After heating for 30 min, the solution is cooled in an ice-bath and filtered under suction to remove the precipitated white crystalline product. Additional crystals may be obtained on evaporation of the ethanolic solution and further recrystallization from ethanol. A 50% yield is typical. *Anal.* Calcd: C, 43.4; H, 4.2; N, 8.4. Found: C, 43.5; H, 4.3; N, 8.3.

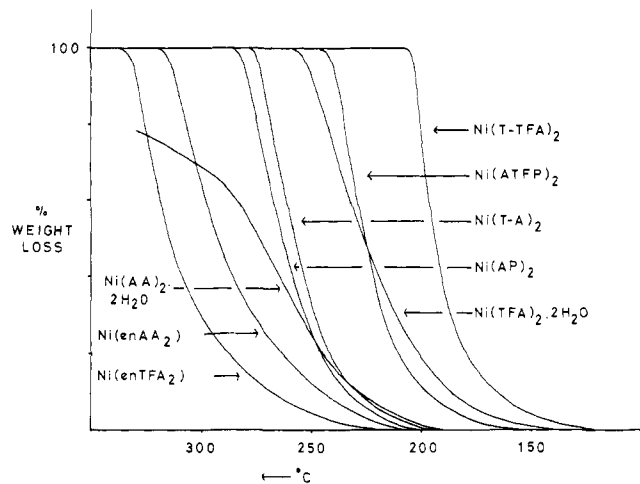


Figure 2. Thermograms of Ni(II) β -diketonates, monothio- β -diketonates, bidentate and tetradentate β -ketoamine chelates

2-mg samples. Heating rate 5°C min^{-1}

β -Diketones. These may be obtained commercially or readily prepared by condensation of appropriate esters and ketones (1). Purification is straightforward.

Mono-thio- β -diketones. These ligands are prepared by the reaction of dry hydrogen sulfide at -70°C with an ethanolic solution of the appropriate β -diketone previously saturated with dry hydrogen chloride gas (14). The relatively low yields of the reactions (typically 20–30%) present a problem which has not presently been overcome. The ligands are best isolated and stored as the lead chelates since they are subject to hydrolysis in the free state. Regeneration of the free ligand is accomplished by passing dry hydrogen sulfide into an ethereal lead chelate solution; the free ligands may be kept at 0°C in hexane solution for some weeks without decomposition and reacted directly in solution (17).

The alternative procedure of Bayer (18) for the preparation of hexafluoromonothioacetylacetone through the intermediate formation of 2-chloro-1,1,1,5,5,5-hexafluoro-4-oxopentene is also lengthy and gives relatively low yields of ligand.

Formation of Divalent Transition Metal Chelates. Bidentate bis- β -Ketoamine Chelates. For the preparation of pure chelates of Ni(II) and Cu(II) in quantities sufficient for full characterization, a convenient procedure involves refluxing an ethanol solution of the β -ketoamine with an excess of freshly prepared metal hydroxide, good yields being obtained after several hours reaction. This procedure is to be preferred over the reaction of the β -ketoamine with a metal-amine complex in aqueous solution where the ammonia (or other free amine) may induce breakdown of the ligand or may compete for the metal ion. The latter problem is particularly severe for the nickel chelates and for all alkylamino ligands such as 4-methylamino pent-3-en-2-one (24). In fact, nickel chelates of the latter ligands cannot be obtained in aqueous solution (19).

Palladium(II) and platinum(II) chelates are best prepared by refluxing the ligands in benzene solution with the metal chloride/benzonitrile complex (e.g., $\text{PdCl}_2\text{C}_6\text{H}_5\text{CN}$) which is previously prepared by refluxing chloride and benzonitrile in benzene.

Once the specific metal chelate of interest has been isolated, purified, and characterized by gas chromatography, thermal analysis, microanalysis, mass spectrometry, etc., it can be used to set up an absolute scale of gas chromatographic response which may be used for comparison purposes in the development of a viable quantitative analytical procedure for the metal in question.

Such a procedure for the reaction of Ni(II) and Cu(II) ions with (H)ATFP is as follows: To a solution of the ligand in a 1:1, ethanol:chloroform solvent is added Cu^{2+} or Ni^{2+} in aqueous solution. The pH of the solution is raised to 10.5–11.0 with sodium hydroxide solution (commercial reagent-grade sodium hydroxide may first be preextracted with the ligand to remove ppm levels of copper and nickel). Precipitation of the metal hydroxides occurs and is considered a prerequisite for the quantitative formation of

(24) R. Belcher, M. Pravica, W. I. Stephen, and P. C. Uden, unpublished work, Birmingham, 1970.

the metal chelates in the ethanolic chloroform phase. Ammonia interferes with complexation because of competition with the β -ketoamine and cannot be used to adjust the pH.

Tetradentate β -Ketoamine Chelates. Similar preparative methods are available as for the bidentate chelates (22), the greater stabilities of the tetradentate chelates reducing problems of hydrolysis or ligand competition.

The preferred procedure for the quantitative formation of Cu(enTFA₂) and Ni(enTFA₂) to the nanogram level is as follows (Ammonia does not interfere with quantitative reaction as for the bidentate β -ketoamine, presumably because of the much greater predicted stability and formation constants for the tetradentate β -ketoamine).

Aqueous metal ion solution (1 ml) is mixed with 95% ethanol (2.5 ml). Ammonia gas is passed through the solution until the pH exceeds 11.5 (about 20 seconds of vigorous bubbling). A chloroform solution of the ligand is added (1 ml) and the mixture shaken to form a single phase. After 5 minutes, distilled water is added to induce separation of aqueous and chloroform phases and the chelate is gas chromatographed directly from the latter phase.

β -Diketonates. Cu(II) and Ni(II) β -diketonates are readily prepared from metal ion solutions and the β -diketone (1). Only highly sterically hindered Ni(II) chelates such as that of dipivalylmethane (DPM) (11) can be obtained as the anhydrous monomeric complexes. Pd(II) and Pt(II) β -diketonates are frequently poorly characterized.

Monothio- β -Diketonates. Chelates of Ni(II) are readily prepared from the reaction of aqueous nickel acetate with ethanolic or *n*-hexane ligand solutions, while Pd(II) and Pt(II) chelates are best made by the metal chloride/benzonitrile complex procedure. Co(II), Zn(II), Cd(II), and Pb(II) complexes are prepared similarly to those of Ni(II) (14). Cu(II) complexes of these ligands cannot be readily prepared since reaction with Cu(II) results in oxidation of the ligand and reduction of the metal to Cu(I) giving a mixture of polymeric species.

Quantitative reaction of Ni(II) in aqueous solution is accomplished by (17) buffering to pH 4.6, shaking with the *n*-hexane ligand solution into which the chelate is extracted. Excess ligand must be removed from the organic phase by treatment with 0.01M sodium hydroxide solution.

Gas Chromatography. A range of gas chromatographic conditions have been described for these chelates, but for this discussion, results are reported using either a Pye R instrument (Pye-Unicam, Cambridge, G.B.) or a Perkin-Elmer 990, each equipped with flame ionization and ⁶³Ni electron capture detectors. Various stationary phases and supports are used, columns are either 1/8-in. o.d. stainless steel or 3/8-in. o.d. Teflon (Du Pont).

Thermal Analysis. Thermogravimetric curves are recorded on either a Du Pont 950 thermogravimetric analyzer or a Perkin-Elmer TGS.1 instrument as noted.

RESULTS AND DISCUSSION

Thermal Properties of Divalent Metal Complexes. It has been recognized since the earliest investigations of volatile metal chelates that a prerequisite for quantitative gas chromatography is the complete volatilization of the complex without thermal decomposition. Thermogravimetric analysis provides this information readily as well as indicating the relative volatilities of different species. It must be emphasized however that complete volatilization does not ensure ideal gas chromatographic behavior as the vapor is further exposed to possible decomposition on the column walls or on the support material or stationary phase. Decomposition may also occur in a heated injection port and elution behavior may be further complicated by nonlinear isotherms producing peak asymmetry. Metal chelates are indeed good examples of the problems involved in the gas chromatography of labile compounds generally.

It is useful, however, to predict chromatographic parameters necessary for viable elution by comparison of thermograms of various chelates. Figure 1 shows thermograms of Cu(II) β -diketonates, bidentate and tetradentate β -ketoamine chelates. Figure 2 shows similar relationships for nickel complexes and includes also monothio- β -diketonates. General trends are clear from these thermograms. With the exception of both acetylacetonates which show

decomposition, all chelates sublime completely, including even the hydrated (and polymeric in the solid phase) Ni(II) β -diketonates which however show an extended sublimation temperature range possibly due to partial or complete water loss during vaporization.

For the Cu(II) chelates, in the case of bis-bidentate species, fluorinated complexes exhibit higher volatility than their nonfluorinated analogs. This trend is somewhat surprisingly reversed, however, for the tetradentate chelates. A general order of volatilities emerges from this and parallel studies on similar systems. Decreasing volatility is shown through fluorinated β -diketonates, fluorinated β -ketoamine chelates, nonfluorinated β -ketoamine chelates, nonfluorinated tetradentate and fluorinated tetradentate chelates. It is possible also to draw a fairly accurate parallel between difference in sublimation temperatures and the column temperatures needed for practicable gas chromatography.

For the nickel complexes, fluorinated monothio- β -diketonates and β -ketoamine chelates are the most volatile followed by their nonfluorinated analogs, respectively; the tetradentate chelates are less volatile and exhibit the same volatility reversal as the copper species. Similar thermal data can be presented for Pd(II) and Pt(II) complexes.

From these thermal data, it might be predicted that Cu(II) β -diketonates, particularly the highly fluorinated species such as Cu(HPM)₂ (HHPM = 1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-octan-4,6-dione, also abbreviated as Hfod) would be preferred complexes for copper determination while Ni(II) mono- β -diketonates would be preferred for nickel. A number of factors, however, are neglected in drawing this conclusion, namely, unpredictable column interactions, decomposition in the vapor phase and the problem of resolution of the complex peaks from the solvent tails at high sensitivities—a practical problem of key importance in gas chromatography. Since ligand availability and purity, quantitative complex formation, hydrolytic stability, etc. are also of importance in analytical technique development, it is clear that quantitative gas chromatography cannot be predicted from thermograms alone, despite their considerable usefulness.

Stability of the Divalent Metal Chelates. From general trends holding in coordination chemistry, it may be predicted that for metals which have considerable class 'b' character such as the nickel group (25,26), more stable complexes are formed with the second or subsequent donor atoms in the groups N < P < As < Sb and O < S < Se < Te. Thus, enhanced thermal stability of the monothioacetylacetonates over the analogous β -diketonates is not unexpected. The absence of hydration or polymerization is further responsible for the enhanced volatility of the sulfur analogs.

This relative order of stability is predictably reversed for metals of class 'a' character in higher oxidation states which also often tend to oxidize monothio- β -diketone ligands to disulfides. The relative thermal stability of analogous oxygen and nitrogen chelated systems is rather more difficult to predict although in general enhanced stable nitrogen chelation tends to increase from left to right in a period. In many cases for nickel and copper, nitrogen chelation is preferred. A large stability increase however is predicted in going from bis-bidentate to tetradentate systems, order of magnitude increases in formation and stability constants often being observed (27).

(25) S. Ahrland, J. Chatt, and N. R. Davies, *Quant. Rev.*, **12**, 265 (1958).

(26) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

(27) A. Ringbom, "Complexation in Analytical Chemistry," Wiley-Interscience, New York N.Y., 1963.

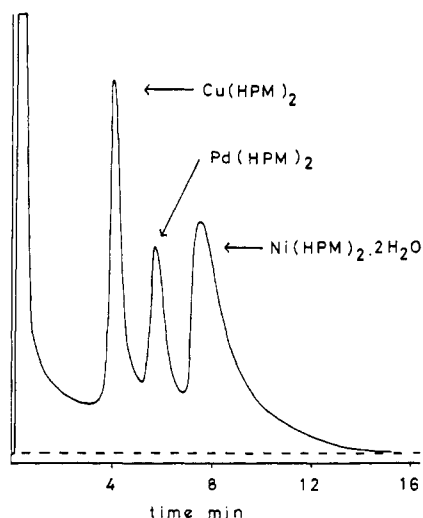
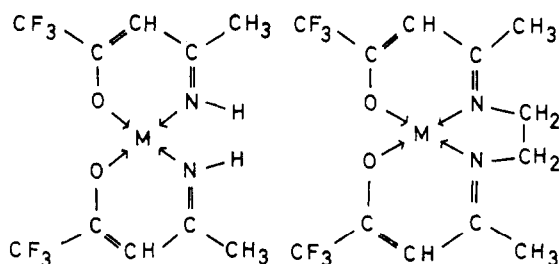


Figure 3. Gas chromatographic separation of Cu(II), Ni(II), and Pd(II) heptafluorobutanoylpivalylmethanates

10 μ g of each chelate in chloroform solution. Column 6-ft Teflon, o.d. $\frac{1}{8}$ -in. at 170 °C. Stationary phase 3% E.301 silicone gum on 60–85 mesh Universal B support



Thus, from the standpoint of the coordinating ligand atom, it might be predicted that increasing stability for the nickel group and copper chelates would occur from β -diketonates, through bidentate β -aminoketonates and β -thioketonates to tetradentate β -aminoketonates, this being modified for copper by redox reactions of the sulfur chelates. Further, the general enhanced stability of fluorinated over nonfluorinated complexes would be expected.

It is this stability order which appears to have the greatest bearing on GC viability in addition to the direct thermogravimetric data.

Gas Chromatography. As in any gas chromatographic analysis, the objectives in metal chelate gas chromatography are quantitative response over an optimal range limited only by detector linearity or other instrumental parameters; linear partition isotherms over a wide concentration range giving gaussian peaks and high column efficiencies; minimal interaction with support or column materials giving rise to decomposition or peak tailing; minimal experimental complexity resulting from the need for special stationary phases, highly deactivated supports or unusual and expensive column materials and treatment.

In many cases, metal chelate gas chromatography has fallen short in some or all of these respects, thus reducing its effectiveness as a competitive analytical technique. For β -diketonates, with the exception of Cr(III), Al(III), Be(II), and a few other complexes, substantial column interactions are observed even when using glass or Teflon columns and deactivated supports, resulting in peak asymmetry, spurious peaks, sample loss, etc. Usually quantitative analysis below the microgram level is difficult and resolution of mixtures often impracticable.

Considering specifically the divalent transition metal

β -diketonates, efforts have been largely unsuccessful except for some Cu(II) complexes. Gas chromatography of the highly substituted Ni(II) and Pd(II) heptafluorobutanoylpivalylmethanates has been achieved but undesirable stationary phase interactions are troublesome (12). Dipivalylmethanates have received attention but appear to show insufficient stability for quantitative trace analysis (28).

The typical gas chromatographic behavior of heptafluorobutanoylpivalylmethanates is shown in Figure 3. A 6-ft Teflon column, o.d. $\frac{1}{8}$ -in. is used at 170 °C employing E.301 methyl silicone gum on 60–85 mesh Universal B (a silanized diatomaceous support). Sample quantities are approximately 10 μ g of each chelate in 1 μ l chloroform and peak shapes are similar to those obtained for injections of individual chelates. Considerable tailing is observed for each complex, particularly for Ni(HPM)₂·2H₂O which is eluted after Pd(HPM)₂ as a result of its hydration. Even under these optimal conditions, quantities of less than 0.2–0.5 μ g of chelate are not eluted.

The substitution of stainless steel or copper columns for Teflon or glass results in almost complete loss of chelate. Other more polar stationary phases also appear to absorb and/or decompose these complexes.

Monothio- β -Diketonates. To the present time, gas chromatographic studies have been largely centered on the nickel group, although promising results have also been noted for Zn(II), Co(II), and Co(III) complexes. While the relative difficulty of preparing and handling monothio- β -diketone ligands is to some extent a practical drawback, excellent quantitative determination of nickel as the monothiotrifluoroacetylacetonate has proved possible. Employment of a ⁶³Ni electron capture detector has enabled nickel solutions in the range of 0.01–0.001 μ g ml⁻¹ to be analyzed quantitatively and linear response is noted in the 1–100 pg range. Quantitation of Pd(II) and Pt(II) should also prove possible with this or similar ligands.

It is of interest that the optimal pH for nickel chelate formation and extraction is 4.5–5.0 but Cu(II), Co(II), and Hg(I) and (II) interfere and must be removed prior to analysis. It seems possible that Co(II) and Ni(II) might be determined simultaneously but the Cu(II) complexes are too readily decomposed for gas chromatographic analysis.

β -Ketoamine Chelates. It cannot be stressed too strongly that there are numerous factors involved in the development of a viable analytical procedure for metal analysis by chelate gas chromatography. Simplicity and reproducibility are essential to methods which are to be superior or competitive with existing approaches. Simplicity is an inherent advantage of gas chromatography provided that analytical parameters are not unduly complex, but preliminary chemical steps must also be uncomplicated both in regard to ligand preparation and quantitative complex formation; reaction conditions should be readily reproduced and interferences minimized. Then the strength of the GC approach in terms of high sensitivity for small volume samples and separative ability can be better realized.

Data are presented for the quantitative analysis of Cu(II) and Ni(II) by β -ketoamine chelate formation, a comparison being made between bis-bidentate and tetradentate complexes. The ligands (H)ATFP and H₂(enTFA₂) are discussed as representative of the two classes. Both ligands are very easily prepared in a pure form by simple laboratory procedures and may themselves be checked gas chromatographically for analytical purity at the levels

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

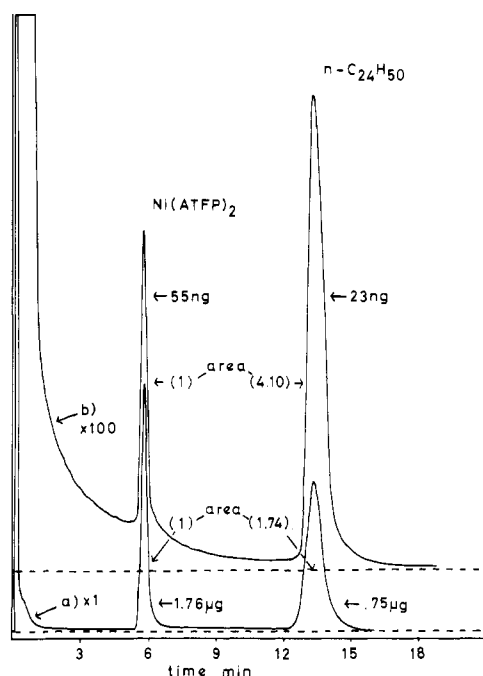


Figure 4. Relative gas chromatographic responses for Ni(ATFP)_2 and n -tetracosane

6-ft \times $\frac{1}{8}$ -in. o.d. stainless steel column at 150 °C. Stationary phase 3% QF 1 fluoropropyl silicone oil on Varaport 30 80–100 mesh. Helium flow rate 58 ml min⁻¹

needed for trace analysis. $\text{H}_2(\text{enTFA}_2)$ shows no evidence of decomposition after prolonged storage but (H)ATFP shows some tendency to decompose to yellowish materials after some weeks or months unless kept desiccated; it may readily be re-purified by silica gel chromatography however.

Figures 4 and 5 show representative chromatograms of Ni(ATFP)_2 and Cu(ATFP)_2 , respectively. n -Tetracosane is included in all chromatograms as an internal standard for purposes of response comparison. Calibration curves for the three compounds are compared in Figure 6 for samples in the 10-ng to 10- μ g range. The chelate standards used are derived from purified complexes.

It is at once apparent that for the gas chromatographic conditions employed, (a 6-ft \times $\frac{1}{8}$ -in. o.d. stainless steel column packed with 3% QF.1 on Varaport (80–100 mesh, column temperature, 150 °C) the behavior of the nickel and copper chelates differs appreciably. Predictably linear response is shown for n -tetracosane over this range, linearity also holding for larger sample sizes. The nickel chelate response is also linear above 10 μ g, the absolute response ratio with respect to n -tetracosane being ca. 1:3.8. Miyazaki *et al.* also observed linear response for the nonfluorinated nickel analog in the 20–200 μ g range (20). Below 10 μ g, the response ratio begins to decrease having fallen to ca. 1:10 in the 10-ng region. A reproducible calibration curve is obtained however although a degree of sample loss is apparent. Figure 4 compares chromatograms at a 32-fold sample size difference. On this column, samples below ca. 5 ng of chelate (1 ng of nickel) give no response, being completely adsorbed or decomposed. It is noteworthy that this detection limit depends somewhat on instrumental design features; thus on transferring this column to a Perkin-Elmer 881 instrument having a steel 'tee' injection port of higher dead volume than the Perkin-Elmer 990, the smallest sample to give any response is ca. 20 ng. It is probable that the use of an all-glass system for this and other chelates will reduce detection limits considerably.

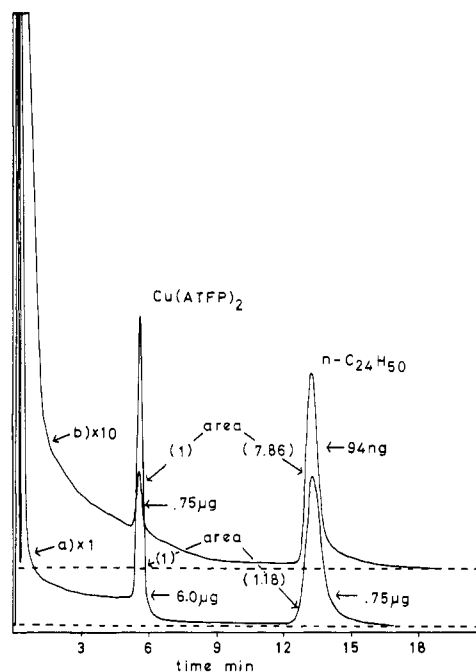


Figure 5. Relative gas chromatographic responses for Cu(ATFP)_2 and n -tetracosane

6 ft \times $\frac{1}{8}$ -in. o.d stainless steel column at 150 °C. Stationary phase 3% QF 1 fluoropropyl silicone oil on Varaport 30, 80–100 mesh. Helium flow rate, 58 ml min⁻¹

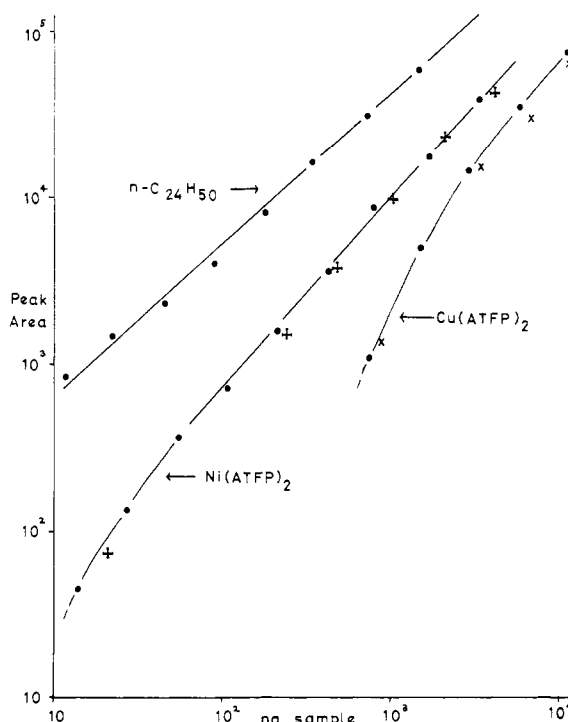


Figure 6. Detector response for Ni(ATFP)_2 , Cu(ATFP)_2 , and n -tetracosane

• Pure standards, + Ni(ATFP)_2 derivatized from aqueous solution, \times Cu(ATFP)_2 derivatized from aqueous solution

It might be predicted that the similarity between analogous nickel and copper chelates would lead to identical response in the flame ionization detector. While the higher molar response of n -tetracosane in comparison with the chelates is not unexpected because of its high carbon content, an absolute response ratio of ca. 1:3.8 might also be predicted for Cu(ATFP)_2 . Such a response is not ob-

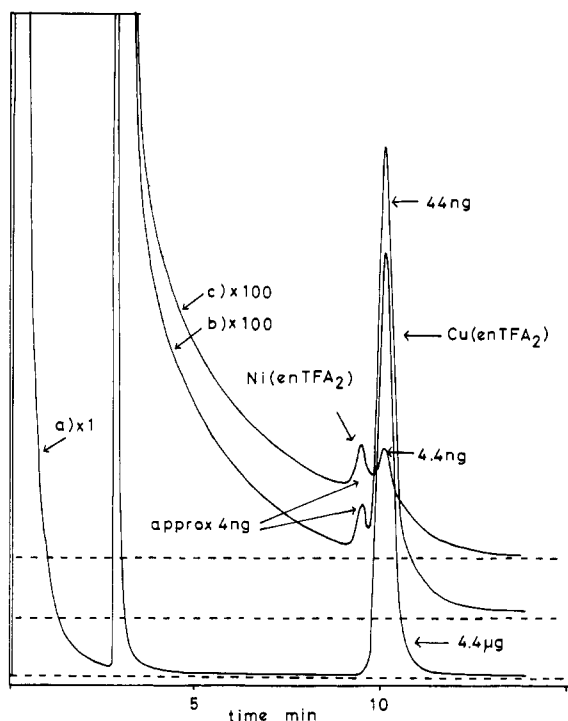


Figure 7. Gas chromatograms of $\text{Cu}(\text{enTFA}_2)$ and $\text{Ni}(\text{enTFA}_2)$

6-ft \times $\frac{1}{8}$ -in. o.d. stainless steel column at 220 $^{\circ}\text{C}$. Stationary phase 3% QF 1 on Varaport 30, 80–100 mesh. Helium flow rate 60 ml min^{-1}

served, however, even above 10 μg . Much larger samples were not analyzed but at the 12- μg level, a response ratio to *n*-tetracosane of ca. 1:10 is noted. The trend of this response, however (Figure 6), is to tend toward that of the nickel chelate at higher concentrations. A very rapid loss of response is noted for $\text{Cu}(\text{ATFP})_2$ below ca. 6 μg and quantities smaller than 0.5 μg were completely lost under the quoted conditions. Spectrophotometric evidence (24) indicates that little decomposition occurs in chloroform solution, so loss must be attributed to column interactions. The behavior of $\text{Cu}(\text{ATFP})_2$ is thus closely similar to that of many fluorinated copper β -diketonates in this respect.

Figure 6 also shows results for Ni and $\text{Ni}(\text{ATFP})_2$ and Cu as $\text{Cu}(\text{ATFP})_2$ formed by chelation of standard metal ion solutions as described earlier. The nickel data shows reasonably good agreement with the calibration curve as derived for pure chelate solutions. Copper data are more erratic, but follows the calibration curve quite accurately.

With respect to the resolution of $\text{Cu}(\text{ATFP})_2$ and $\text{Ni}(\text{ATFP})_2$, little real potential is apparent. While a small difference in thermograms is noted, retention times on the QF 1 column (and other stationary phases suitable for elution of these chelates) are virtually identical. From comparison with the behavior of the tetradentate chelates, QF 1 appears to be the most likely phase to be effective. This does not rule out the possibility that other β -ketoamine ligands may show greater resolution, for example the non-fluorinated analogs show a greater difference in volatility and retention time (20) but unfortunately their thermal stability is also lower.

Preliminary data for the palladium(II) and platinum(II) chelates of $\text{H}(\text{ATFP})$ and similar ligands (29) also appears very promising. Both appear to show similar or greater stabilities and detection limits to the nickel chelates and there is also evidence of some increase in molar response. Thus, in terms of metal analysis by chelate gas chroma-

(29) R. Belcher, A. Kamalizad, R. J. Martin, W. I. Stephen, and P. C. Uden, unpublished work, Birmingham and Amherst, 1970–72.

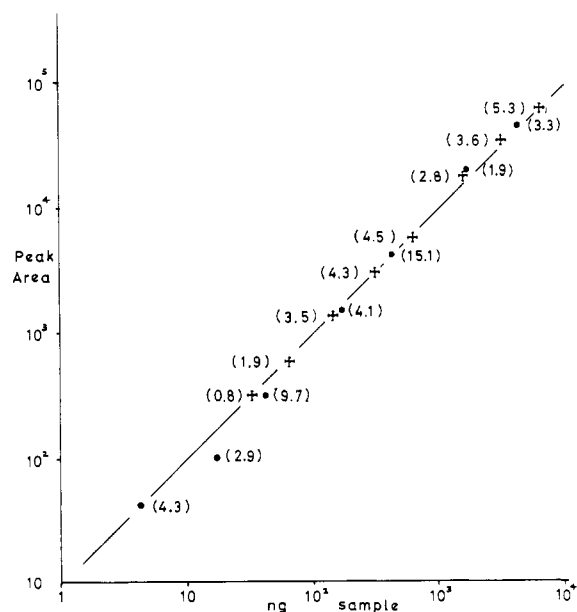


Figure 8. Detector response and relative standard deviation values for $\text{Cu}(\text{enTFA}_2)$ and $\text{Ni}(\text{enTFA}_2)$

● $\text{Cu}(\text{enTFA}_2)$, + $\text{Ni}(\text{enTFA}_2)$

tography, the bidentate β -ketoamines appear viable for the nickel group down to the nanogram metal level, a limit which may well be extended for glass columns and electron capture detection. Copper β -ketoamine detection limits are unlikely to be much improved however.

Figure 7 shows chromatograms for $\text{Cu}(\text{enTFA}_2)$ as formed from standard aqueous solutions of Cu^{2+} ion and excess $\text{H}_2(\text{enTFA}_2)$ under the reaction conditions noted previously. Curves are shown at three different sample concentrations, relative detector sensitivities being noted. For comparison purposes, the two chromatograms show peaks for $\text{Ni}(\text{enTFA}_2)$ formed quantitatively under the same conditions from Ni^{2+} present in the reactant solution used at approximately the 0.15-ppm level. Although quantitation for nickel has not yet been carried out in detail to this level, it appears that linearity of reaction and response are still maintained. Such trace levels of copper and nickel must first be removed from reagents for work at this level; pre-extraction with the ligand solution is again a preferred method.

The presence of a large ligand excess (typically 100- to 1000-fold) for the low metal concentration level reactions presents some problems in that ligand tailing at high sensitivities is added to solvent tailing. Even so the present data show reasonable values of relative standard deviation, and current work indicates that ligand concentrations may be drastically reduced at this level without reducing reaction efficiency.

Figure 8 shows a plot of relative peak area response in the range of 4–7000 ng for both $\text{Cu}(\text{enTFA}_2)$ and $\text{Ni}(\text{enTFA}_2)$, prepared from standard aqueous metal ion solutions. A series of three reactions was carried out for 1 ml of each standard solution, the Cu^{2+} concentrations ranging from 0.15 to 150 ppm and the Ni^{2+} concentrations from 1.18 to 236 ppm. The resultant chloroform chelate solutions were analyzed by triplicate chromatographic injections and peak areas determined by planimetry. The plot shows the mean peak area obtained for each sample together with values for relative standard deviations. The latter values are below 5% for most samples. Errors in injection and planimetry are not included in detail but probably contribute 2–3% in combination to the given

values. It is important to note that the precision at low chelate levels is of the same order as that for high level samples. The two high deviation values for copper are possibly due to some loss of chloroform during the ammonia treatment of the solution. It is also noteworthy that in addition to being linear over the range reported, the plots for copper and nickel are superimposed, thus substantiating the idea of identical detector responses to the two complexes. This is in clear contrast with the data for the bidentate β -ketoamine complexes where loss of copper chelate prevented such a conclusion being drawn.

From many points of view, the tetradentate β -ketoamine chelates appear to hold out the best prospects for the determination of sub-nanogram samples of nickel, copper, palladium, and platinum. Their stability is such that it is probable that linear response can be extended to the picogram range using glass columns and electron capture detection. One possible problem to be overcome is the tailing from excess ligand. This difficulty will be lessened for Pd and Pt because of their greater separation from the lig-

and. Such studies are currently in progress. It is also clear that complete resolution of copper and nickel chelates is essential for quantitative determination of both ions. While $H_2(enTFA_2)$ gives satisfactory results for each chelate in the presence of up to a tenfold excess of the other, other ligands in this series, notably the propylenediamine analog, (22) show improved resolution.

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