

Use of Negative Chemical Ionization Mass Spectrometry for the Trace Analysis of Metals

by Terence H. Risby*

The synthesis of various volatile and thermally stable derivatives of metals ions has permitted the use of conventional mass spectrometry for trace metal analysis. This paper reviews the development of the field using electron impact and chemical ionization mass spectrometry. This latter methodology produces simple mass spectra that enable complex mixtures to be analyzed. In addition the use of negative ion detection has produced selective ionization since many metal chelates contain heteroatoms which are electronegative.

A discussion of the use of this general methodology for trace metal analysis is included, together with its applications to the analysis of ruthenium in automobile exhaust emissions and iron in red blood cells from laboratory rats. The future use of this methodology is expected to be for the monitoring of stable metal isotopes. This procedure could be used to follow these tracers in clinical and environmental studies and it is expected that their use will replace radioactive isotopes in most studies.

Trace concentrations of metals are currently receiving considerable interest as a result of their significance in environmental and health-related studies. Metals are nutritionally required by biological systems for normal growth and some of these metals at higher or lower concentrations can cause detrimental effects either as metallic imbalances or as deficiencies. Other metals have been implicated in various clinical conditions such as poisoning and carcinogenesis. Metals play a significant role in man's environment, since they are found in air, water, and soil and therefore can affect both flora and fauna. The sources of metals are both natural and anthropogenic and as a general rule the latter sources present greater problems since these metals can be in environmentally significant forms ($< 3.0 \mu\text{m}$ sized particles or soluble particles) (1). Other applications which require methods of analysis for trace metals include the determination of metals in used lubricating oils, in foods, in geological samples, and for assaying precious alloys.

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Gas Chromatography of Metal Complexes

The use of gas chromatography and/or mass spectrometry for the analysis of trace concentrations of metals has enjoyed considerable support during the past twenty-five years. Lederer, in 1955, was the first to suggest that certain neutral metal complexes may be suitable for separation by gas chromatography (2). In this classic paper, some metal 2,4-pentanedionates were shown to have sufficient volatilities and thermal stabilities (Be, Al, and Cr) to maintain their integrities in gas chromatographic columns. However, while this paper did propose this novel method of analysis for metals it was not until Sievers and Uden and their respective co-workers reported on additional complexes and complexing agents that the major breakthrough in this area occurred. (3-7) These workers found that the introduction of heteroatoms such as fluorine into β -diketones increased the volatility and thermal stability of the resulting complexes. Examples of these ligands are shown in Table 1. Some of these ligands have bulky R groups attached to sterically hinder coor-

Table 1. Anions of β -diketones.

$\begin{array}{c} \text{R} - \text{C} - \text{CH} = \text{C} - \text{R}^1 \\ \parallel \quad \quad \\ \text{O} \quad \quad \text{O}^{\theta} \end{array}$		
R	R ¹	
CH ₃ -	CH ₃	2,4-pentanedionato (acac)
CF ₃ -	-CH ₃	1,1,1-trifluoro-2,4-pentanedionato (tfa)
CF ₃ -	-CF ₃	1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hfa)
CF ₃ CF ₂ CF ₂ -	-C(CH ₃) ₃	1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato (fod)
(CH ₃) ₃ C-	-C(CH ₃) ₃	2,2,6,6-tetramethyl-3,5-heptanedionato (thd)
CF ₃ CF ₂ -	-CF ₂ CF ₃	1,1,1,2,2,6,6,7,7-decafluoro-3,5-heptanedionato (dfhd)

dination sites in metals which have a greater number of coordination states than oxidation states. If these groups were not bulky, the resulting metal β -diketonates would be hydrated and exhibit low thermal stabilities. Various comprehensive reviews have been published which discuss the development of this field in detail (3-7). Another approach to saturating coordination sites has been to use mixed ligand complexes of hexafluoroacetylacetone (hfa) and tributyl phosphate or hfa and dibutyl sulfoxide (8,9). An additional advantage of these reagents are that they increase the efficiency of solvent extraction of the metals from aqueous solution. The use of the β -diketones ligands has generally been more successful with trivalent metals than with divalent metals and various workers have attempted to remedy this deficiency. Livingstone, Uhlemann, and Beyer and their respective co-workers (9-11) have substituted sulfur atoms for the oxygen atoms in β -diketones in attempts to produce complexing agents for the class B metals. Although this approach is reasonable, there are many difficulties which are associated with the ease of the formation of ligands and with the quantifications of the resulting complexes (9-11). Complexes based on β -ketoamines are another approach which has been attempted, notably by Uden and co-workers, and both the bidentate and the tetradentate β -ketoamines have been studied. Although the bidentate ligands are more general in application, the tetradentate complexes were found to have superior characteristics and produced complexes for divalent metals which do not generally form volatile β -diketonates (7).

On the basis of all the published data, Uden et al. have drawn the following conclusions (7). Although a number of metal complexes have been

separated by gas chromatography, only beryllium, chromium, and possibly aluminum β -diketonates can be separated quantitatively at trace or ultratrace levels and can be used for analytical determinations. Analytical methodologies involving use of β -ketoamines have been developed for copper, nickel, and palladium, although complete analytical methodologies have not been substantiated. Most of the problems which have been experienced with the use of gas chromatography for metal analysis have been the result of column reactivity which causes irreversible adsorption of the metal complexes and limits detection limits to around 10^{-6} g.

Mass Spectrometry of Metal Complexes

Electron Impact Mass Spectrometry

Positive Ions. The sample requirements of mass spectrometry with conventional gas phase ionization methodologies are very similar to those for gas chromatography. This is evident from the current popularity of gas chromatograph-mass spectrometer systems, for the effluent from a gas chromatographic column is an ideal inlet for mass spectrometers. However, mass spectrometers have the advantage that other methods of sample introduction are also well-established and these methods are not as sensitive to sample nonvolatility and thermal instability.

The first mass spectrum of a β -diketonate [Cr(acac)₃] was reported by McLafferty in 1957 (12). Several years later, MacDonald and Shannon presented a detailed study of the electron impact (EI) mass spectrometry of the transition metal acetylacetonate complexes (13) and the metal complexes of 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, DPM) (14). These workers observed novel modes of fragmentation which were related to the normal oxidation states of the metals under study and introduced the concept of valence change in the mass spectra of metal complexes (15). This concept was reviewed several years later after a wealth of spectral data had accumulated (16). Later EI mass spectrometric studies of these metal complexes included the Acac (17), derivatives of beryllium complexes (18), partially fluorinated metal complexes of transition metals (19), and the alkaline earth metals (20). The results of these studies have led to more detailed investigations of the energetics (appearance potential data) of metal chelate ionization by Westmore and Reichert and others (21-

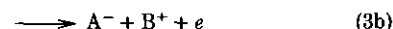
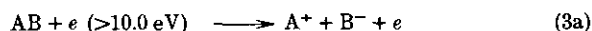
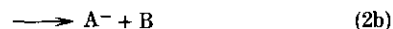
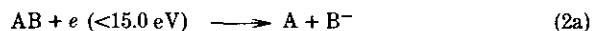
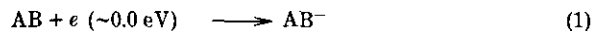
26). Also the energetics of fragmentation of the β -diketonates have been reviewed (27).

In 1967 Jenkins and Majer introduced a technique for quantifying the metal concentrations (in the form of their metal chelates) by EI mass spectrometry. These researchers used the integrated ion current (IIC) methodology in which the mass spectral region of the most abundant ion of interest was repetitively scanned with concurrent oscillographic recording as the sample was evaporated from the direct insertion probe. A calibration gas (heptacosafuorotri-*n*-butylamine) was used to tune the mass spectrometer (AEI MS 50) in the mass region of interest. Nickel dimethylglyoxime was used in this initial study (28) and in subsequent studies the oxines of several transition metals were investigated (29, 30). Detection levels for nickel were reported in the picogram range while those of the copper and aluminum oxines were reported in the submicrogram ranges. The same analytical technique was used for studies of the β -diketonate complexes of the rare earths (31) and the alkali metals (32). The effect of source temperature and thermal stability of the chelate on the IIC was reported in one of these studies (32). The determination of copper as the $\text{Cu}(\text{acac})_2$ complex has been reported at the nanogram level (33) by use of a deuterated derivative of $\text{Cu}(\text{acac})_2$ as the internal standard. These authors commented on the disadvantages of using a calibration gas without an internal standard as it does not account for irreproducible sample loss by the probe introduction technique. These researchers further developed their trace technique for the analysis of copper and iron using the isotope dilution methodology (34, 35). A brief review on trace metal analysis has discussed the advantages of EI over spark sources mass spectrometry (SSMS) and the use of calibration gases and internal standards in quantitative analysis (36). Related studies which deal with metal-exchange reactions with ligands in the ion source of a mass spectrometer have been observed and discussed (37-39). Applications of the IIC methodologies have appeared in the literature with reference to chromium and beryllium in biological samples (40) and chromium in lunar materials (41). A short review of ultra trace analysis using mass spectrometry of metal β -diketonates has been published (42).

Negative Ions. The substitution of heteroatoms into β -diketonates to produce chelates with enhanced volatility and thermal stability has provided an additional advantage for studies with mass spectrometry. Those atoms produce com-

plexes with increase electron affinities (electron-negativities) which make them more amenable to the formation of negative ions than to the formation of positive ions.

The mechanisms for the formation of negative ions can be resonance capture of electrons, dissociative capture of electrons or ion-pair production [Eqs. (1), (2), and (3)]. The mechanism which dominates is dependent upon the energy of the colliding electron (43).



Under typical EI conditions ion-pair production is expected to dominate since the primary electron-beam (70 eV) is not moderated to low energies by collisions at low pressures.

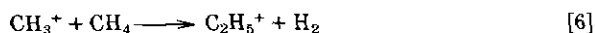
Many studies have reported on negative ion mass spectra (70 eV) of molecules which contain heteroatoms and in general the resulting negative ion mass spectra (EI) are less complex than the positive ion mass spectra (EI) under identical conditions. The first studies to use negative ion mass spectrometry for metal compounds were by Svec and co-workers. In these studies a modified mass spectrometer, which could simultaneously detect both negative and positive ions, was used to monitor the halides and oxyhalides of chromium, vanadium, titanium, and silicon (44, 45). The predominant mechanisms for the formation of these negative ions by collisions with electrons were shown to be resonance capture or dissociative capture. The results indicate that at EI pressures (10^{-5} torr) the electron beam is either moderated to around 10 eV or else the primary electron beam has a wide energy distribution. These mechanisms account for the simplicity of the observed mass spectra since these ionization processes do not fragment the molecule. A recent comparison of negative and positive ion mass spectrometry has shown that the expected selectivity of ionization to produce negative ions is observed for particular classes of molecules (46).

Recently negative ion mass spectra of various fluorinated metal β -diketonates have been reported (47-49) and the results obtained with these studies parallel those obtained for other molecules which contain heteroatoms. Although an obvious advantage is accrued by the use of negative ion mass spectrometry in terms of simplicity and selectivity no major use has been made

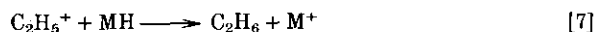
of this technique for qualitative or quantitative analysis. This is probably the result of the popularity of chemical ionization mass spectrometry and the nonavailability of commercial negative ion mass spectrometers.

Chemical Ionization Mass Spectrometry

Positive Ion. Chemical ionization mass spectrometry is a methodology which evolved from high-pressure mass spectrometric studies of ion-molecule reactions of methane at the Esso Research and Engineering Company (now Exxon) by Field and Munson in 1966 (50). This methodology has an ion source which contains a high pressure of a reactant gas (typically methane at a pressure of 0.5–2.0 torr) which is ionized by collisions with high energy electrons (~ 1 keV) [Eq. (4)]. These primary ions react with additional reactant gas molecules by ion-molecule reactions to form a set of secondary reactant ions [Eqs. (5) and (6)].



The ions CH_5^+ and C_2H_5^+ compose about 90% of the total ion current for methane and these ions interact with the sample molecules, present in a ratio 1 to 1000 compared to the reactant gas, to produce sample ions by hydride abstraction or by proton transfer [Eqs. (7) and (8)].



These reactant ions can be viewed as gas phase Lewis or Brønsted acids. The exothermicity of these reactions [Eqs. (7), (8)] are dependent upon the relative proton affinities of the reactant and sample ions and therefore, selectivity of ionization can be obtained by the judicious selection of reactant gas. The chemical ionization mass spectra of sample molecules are typically simple and they often consist of the molecular ion (M^+ or MH_2^+ with little concomitant fragmentation. Therefore, chemical ionization mass spectrometry has enjoyed considerable application in the areas of quantitative and qualitative analysis (51–53).

The chemical ionization mass spectra of the lanthanide tris-2,2,6,6-tetramethyl-3,5-heptanedionates and tris-1,1,1,2,3,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionates were the first mass spectra to be reported (54, 55). These compounds were chosen since the electron impact mass spectra of mix-

tures of these complexes are difficult to analyze as a result of the fragmentation which occur upon ionization.

In contrast, the chemical ionization mass spectra showed no fragmentation in the region of the molecular ion except for the $\text{Ln}(\text{fod})_3$ complexes which showed ions of low intensities which corresponded to the loss of 18, 37, or 38 amu. In spite of these minor fragmentations it was possible to deconvolute mixture spectra. No analytical data were obtained for the lanthanides. In a subsequent study (56) the chemical ionization mass spectra of various transition metal chelates of the ligands $\text{H}(\text{tfa})$, $\text{H}(\text{acac})$, and $\text{H}(\text{thd})$ were obtained and the spectra of the nonfluorinated chelates were devoid of fragment ions in the region of the parent molecular ions. However, the fluorinated chelates showed minor fragment ions which correspond to the loss of 20 amu. Sensitivity studies were performed by using $\text{Cr}(\text{tfa})_3$ and the limit of detection was found to be on the order of 8×10^{-13} g of chromium. A novel methodology of direct injection of solutions of the chelate into the chemical ionization source was used and the sensitivities obtained were comparable with previous studies using electron impact mass spectrometry. Methane or isobutane was used as the reactant gas and slightly less fragmentation was observed with isobutane.

The simplicity of the chemical ionization mass spectra is the major reason why this methodology is so useful for the quantitative analysis of metals since it is relatively easy to perform qualitative analysis on the basis of molecular weight and isotopic abundances of the molecular ion.

Currently, there is a major interest in the use of stable isotopes and isotope dilution techniques as tracers for a wide range of applications. However, these studies can not be performed by chemical ionization mass spectrometry since it does not have the required sensitivity. This is the result of the contributions of the various mechanisms which produce the molecular ion to the isotopic abundances of the molecular ion. As a result the molecular ion is a hybrid of three ions (M^+ , MH^+ , and MH_2^+), each with its own natural isotopic abundances. Although the ion intensities of two of these ions (M^+ and MH^+) are minor compared to the protonated molecular ion (1–2%), their presence is pressure-dependent; as a result, accurate isotopic ratios are very difficult to predict. Therefore, negative ion chemical ionization mass spectrometry was considered as a methodology to monitor metals since it does not suffer from interfering mechanisms.

Negative Ions: At chemical ion source pres-

tures there is a distribution of electron energies from 0.0 eV to the energy of the ionizing beam. This distribution of electron energies consists of a large secondary electron current produced by the multiple ionizations of each high-energy primary electron and the moderated primary electrons. Therefore, in addition to ion-molecule reactions, the sample molecules are experiencing collisions with electrons. There is therefore a large probability that the sample molecules could form negative ions, depending upon the relative magnitudes of the cross sections for electron impact as compared to ion-molecule reactions. The resulting negative ions can be used for isotopic dilution methodologies since the molecular ion will not have any contributions from competing ion-molecule reactions.

The first study which used this methodology reported the negative ion chemical ionization mass spectra of various transition metal complexes (Table 2) (57). In all cases, negative ions were observed which correspond to the capture of an electron. In addition, minor ions were observed for the fluorinated metal β -diketonates which corresponded to the association of O_2^- with the sample molecules. These ions disappeared when the reactant gas (methane) was dried by a molecular sieve trap.

A sensitivity study was performed to determine the relative differences in the ion intensities for the formation of negative and the positive ion with a series of chromium β -diketonates. The results of this study are summarized in Table 3. These data clearly show that the presence of electron-withdrawing fluorine atoms increase the probability for the formation of negative ions whereas the methyl or *tert*-butyl groups which are electron-releasing groups increase the probability for the formation of positive ions. The results obtained with $Cr(fod)_3$ are interesting since this

Table 3. Relative sensitivities for negative vs. positive ion modes.

Chelate	Relative sensitivity	
	Positive mode (M+1) ⁺	Negative mode (M) ⁻
Cr(hfa) ₃	1	5000
Cr(tfa) ₃	1	100
Cr(fod) ₃	1	10
Cr(thd) ₃	10	1
Cr(acac) ₃	10	1

chelate has both electron-releasing and electron-withdrawing groups. The data appear to indicate this complex has a slightly increased tendency to form negative ions. A preliminary sensitivity study was performed and it was established that the minimum detectable limit was not improved by detecting negative ions as opposed to positive ions under identical operating conditions. However, this result reflects the stabilities of these complexes at low concentrations rather than the relative sensitivities of the methodologies.

Negative ion chemical ionization mass spectra were obtained of various bidentate and tetradentate β -ketoamines and the β -diketonates of divalent metals and in all cases the major ion corresponded to the molecular ion (58).

In a subsequent study, a complete analytical procedure was developed for the determination of ruthenium in automobile exhaust particulate matter (59) (Table 4). This study showed that the data obtained by using gas chromatography-negative ion chemical ionization mass spectrometry were comparable to those obtained with neutron activation analysis (Table 5).

Also a preliminary procedure has been developed which used negative ion chemical ionization mass spectrometry to monitor the enrichment of

Table 2. Negative ion chemical mass spectra of metal β -diketonates

Complexes on which NICI spectra obtained
Mn(acac) ₂ , Mn(tfa) ₂ , Mn(thd) ₃
Ni(acac) ₂ , Ni(tfa) ₂ , Ni(thd) ₂
Cu(acac) ₂ , Cu(tfa) ₂ , Cu(thd) ₂
Zn(acac) ₂ , Zn(tfa) ₂ , Zn(thd) ₂
Pt(acac) ₂ , Pt(tfa) ₂
Pd(acac) ₂ , Pd(tfa) ₂
VO(acac) ₂ , VO(tfa) ₂
Cr(acac) ₃ , Cr(tfa) ₃ , Cr(thd) ₃ , Cr(fod) ₃ , Cr(hfa) ₃
Fe(acac) ₃ , Fe(tfa) ₃ , Fe(thd) ₃
Co(acac) ₃ , Co(tfa) ₃ , Co(thd) ₃
Ru(acac) ₃ , Ru(tfa) ₃
Rh(acac) ₃ , Rh(tfa) ₃

Table 4. Analytical procedure for determination of ruthenium on membrane filters.

Step #	Procedure
1	Using Teflon tweezers, place Fluoropore filter in a pretreated glass ampule
2	Add 1.0 ml HCl + 2 drops HNO ₃ (ultrapure)
3	Evaporate to near dryness with gentle heat
4	Add 0.5 ml HCl (10%)
5	Add 0.5 ml H(tfa)
6	Reflux for 1 hr
7	Neutralize with K ₂ CO ₃ (25% wt/wt)
8	Add 0.5 ml toluene
9	Seal ampule and shake for 30 min
10	Extract organic layer
11	Inject into gas chromatograph-negative ion chemical ionization mass spectrometer.

Table 5. Results of determination of ruthenium in membrane filters.

Sample	Rg initial, μg	R μ found, μg	
		NAA	CIMS
1	12(as 1,10-phenanthroline)		
2	12(as 1,10-phenanthroline)		
3	10	8.9 ± 0.09	9.2 ± 0.15
4	10	8.6 ± 0.1	9.5 ± 0.26
5	10 + auto exhaust	8.0 ± 0.08	8.2 ± 0.47
6	10 + auto exhaust	8.7 ± 0.1	9.1 ± 0.29
7	1.0	1.0 ± 0.1	0.97 ± 0.08
8	1.0	1.1 ± 0.1	1.0 ± 0.1
9	Auto exhaust only	not detected	not detected
10	Auto exhaust only	not detected	not detected
11	Blank filter	not detected	not detected
12	Blank filter	not detected	not detected

^{54}Fe in rat red blood cells (60,61) (Table 6). This study was designed to develop a methodology suitable for metabolic pathway, metabolic conversion rates, and iron pool size studies in both normal and deceased states. In this study, the amount of ^{54}Fe administered was $\sim 50 \mu\text{g}/200 \text{ g}$ rat, i.e., $\sim 0.148 \text{ g}$ hemoglobin/ml blood and $\sim 0.50 \text{ mg}$ bound Fe/ml blood. A 10-ml sample preparation gives $\sim 57 \text{ ppm}$ iron or $\sim 3.31 \text{ ppb } ^{54}\text{Fe}$ ($\sim 3.0 \text{ ng } ^{54}\text{Fe}/1 \mu\text{l}$). Previous studies indicated absorbed ^{54}Fe will increase the normal ^{54}Fe concentration to $\sim 65 \text{ ppb}$ ($\sim 58 \text{ pg } ^{54}\text{Fe}/1 \mu\text{l}$). Considering absorption extremes of 5-50%, the results in Table 7 are obtained. The results of this study were disappointing, since although the stable isotope methodology was successful the complete procedure failed as a result of difficulty in analyzing Fe (thd)₃ at levels below 10^{-9}g . Table 7 illustrates the necessary sensitivity required for this methodology even though this study was not successful. This lack of sensitivity was caused by the instability of the iron β -diketonates. A recent presentation has confirmed these results using electron impact mass spectrometry (62). Further work in this area is currently directed towards improving

Table 6. Analytical procedure for ^{54}Fe in red blood cells of rat blood.

Step	Procedure
1	Take volume of blood and add heparin
2	Centrifuge blood and separate red blood cells
3	Decant plasma
4	Ash cells with a low temperature asher
5	Add 1-ml HCl
6	Evaporate to dryness
7	Add chelating agent in ethanol
8	Inject into gas chromatograph-negative ion chemical ionization mass spectrometer with a data handling system

Table 7. Calculations involved in using rats to study iron absorption using ^{54}Fe .

Absorption (%)	Increase in ^{54}Fe sensitivity, ppb	Sensitivity needed
5	19	1/172
50	191	1/17

chelate stability since this is the limiting step in the procedure.

In conclusion, negative ion chemical ionization mass spectrometry does appear to offer substantial advantages for the analysis of metals since the resulting mass spectra are simple to analyze. Also this methodology is suitable for tracer studies with stable isotopes. This latter field is developing rapidly, since the use of radioactive isotopes in clinical studies may present unnecessary health hazards.

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