FAST-ATOM BOMBARDMENT MASS SPECTROMETRY AND RELATED TECHNIQUES

JACK MARTIN MILLER

Department of Chemistry, Brock University, St. Catharines, Ontario, Canada

I. Introduction

Mass spectrometry has become a very important tool for the inorganic chemist, having been extensively applied particularly in the fields of organometallic and coordination chemistry (*1–3*). However, for the inorganic chemist dealing with ionic materials, thermally labile systems, or polymeric systems not readily volatilized in the "organic" mass spectrometer (*1*), mass spectrometry remained a dream for a long time. The exceptions were those with access to "inorganic" mass spectrometers, with thermionic and spark sources, designed primarily for elemental analysis or isotope ratio determination and the surface scientists with access to secondary ion mass spectrometers (SIMS), ion microprobes, and related devices. Most of these were low-

ISBN 0-12-023628-1

mass, low-resolution devices, not particularly adaptable to the problems of the inorganic chemist, i.e., problems analogous to those for which the organic chemists have so widely applied mass spectrometry. In addition, there was the widely held belief that SIMS was only applicable to conducting samples and that surface charging effects precluded application to neutral molecules. Early attempts at molecular SIMS suggested that the sample lifetime would also be exceedingly short.

This article deals primarily with fast-atom bombardment (FAB) mass spectrometry. It is basically an outgrowth of SIMS, except that it uses an energetic beam of fast neutral atoms of an inert gas, rather than 2- to 8-keV ions, as the means of sputtering charged species from a surface. This technique, which was readily adapted to high-mass, high-resolution (organic) mass spectrometers, together with the discovery that dissolving the sample in a matrix liquid, such as glycerol, gave long-lived signals, burst onto the mass spectrometry scene in 1980–1981 (*4–9*)—initially finding its greatest application to biological molecules that were polar and thermally labile. However, from the earliest papers on FAB, the inorganic applications were apparent. Since FAB mass spectra were able to show a parent quasi-molecular ion for vitamin B_{12} (*m/z* 1355) and its coenzyme (*m/z* 1579) (*4, 5, 8*), almost everyone with early access to the technique tried these cobalamins as ideal model compounds (*10, 11*). The observation of vitamin B_{12} by mass spectrometry has been described as a "milestone" (*12*). Many people, myself included, saw or used commercial prototype FAB sources before the first paper on the subject (*5*) appeared in print.

Although the growth in applications of FAB has been explosive, inorganic applications have been slower in coming for several reasons. First, as Wilson and I suggested in an earlier review (*1*), the instrumentation seldom belonged to the inorganic chemist and our metals may have been feared by traditional mass spectroscopists. More important, the matrix liquid has been a greater problem in inorganic chemistry, than for the polar organic and bioorganic molecules for which FAB (using a glycerol matrix) had proved so successful. I hope, however, to show that FAB offers great potential for solving problems in inorganic chemistry.

II. The Fast-Atom Bombardment Method

A. BASIC METHODS

The basic method involves the addition of a source of "fast atoms" to a conventional mass spectrometer. This neutral atom beam is directed onto a sample deposited on the metal tip of a direct-insertion probe such that the sputtered ion beam is directed onto the entrance slits of a conventional mass spectrometer. The atom beam usually is directed onto a bevelled probe tip so that it makes an angle of about 60–70° with the surface normal (*13*) and an angle of about 90° with the direction of the spectrometer ion beam. No new instruments have had to be designed for the technique. FAB sources have been retrofitted to both new mass spectrometer designs and to instruments designed more than 20 years earlier. As long as the basic pumping speed of the ion source is fast enough to remove the inert gas coming from the atom gun, and as long as there is a suitable port onto which the gun can be mounted while still providing for a direct insertion probe, any mass spectrometer, including quadrupole mass analyzers, can be retrofitted for FAB, although new source components are required to extract the sputtered ions efficiently. Martin *et al.* (*13*) have published a useful summary of the optimization of the FAB experiment, though Campana (*14*) has reminded the FAB community that most of the factors that have been found optimal for SIMS by surface chemists also apply to FAB, thus demonstrating the similarities of the techniques. Rollgen and Geismann (*118*) have replied, suggesting that things were less obvious than suggested by Campana.

The factor that makes FAB–MS so different from EI–MS is that, in its usual form, the sample coating the probe tip consists of a solution or suspension in a relatively nonvolatile matrix liquid such as glycerol. This provides for a continually renewed surface exposed to the atom beam and thus spectra that are stable over a period of many minutes. No heating of the sample is required other than the localized energy implanted in the sample by the atom beam. Although complications may result from interactions with the matrix liquid, they are often less than, or certainly no worse than, such complications as thermal decomposition or ion molecule reactions, involved in other techniques for sample volatilization. In addition, FAB–MS is looking at condensed-phase systems similar to those investigated by NMR or IR. Thus perhaps the data are easier to correlate. Several reviews or introductions to the method have appeared (*4, 7–9, 13, 15–22*).

B. INSTRUMENTATION

Figure 1 shows schematically the important parts of a FAB source. The atom guns typically can handle argon or xenon, though they have also been used with heavy metal atoms such as mercury (*23*). The heavier the bombarding atom, the greater the sensitivity, which is roughly proportional to atomic weight (*24*). Thus argon is used for

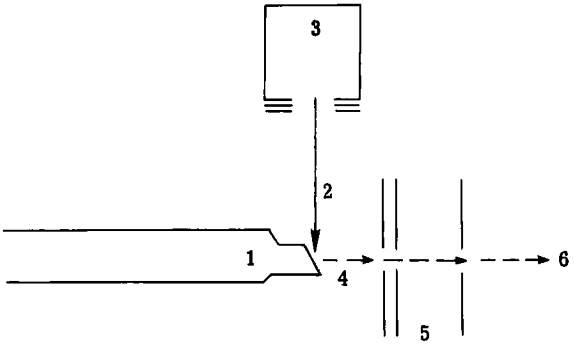


FIG. 1. Schematic diagram of a simplified FAB source: (1) probe, (2) fast-atom beam, (3) atom gun, (4) sputtered secondary ion beam, (5) source ion optics, (6) to mass analyzer.

routine work where sensitivity is good, and xenon for situations where sensitivity is a problem. However, gas consumption is low enough so that, if care is taken, xenon can be used at all times without excessive cost. The guns used are usually commercial models, typically a saddle-field source [e.g., Ion Tech. (*28*)] or Capillaratron [Phasor (*26*)] though home-built systems are also described [e.g., (*26, 27*)]. There are also guns designed to produce beams of Cs ions (*26*). A power supply is needed for the source to provide for voltages of 2–10 keV for acceleration of the ions produced, which are then neutralized by collision to produce the fast atoms. The probe tip is usually metal; copper [which occasionally has been observed to form cluster ions with the sample or matrix (*13*)] or stainless steel are the most commonly used materials. In a magnetic analyzer instrument, the repeller voltage is simply applied to the probe tip. The collimating and focusing electrodes are similar to those in an EI source but with wider spacings, allowing for the greater dispersion of the sputtered ions.

FAB sources readily produce high-mass cluster ions and ions corresponding to high-molecular-weight compounds not previously amenable to study by mass spectrometry. As a result, new magnetic analyzers have been developed that, through the use of nonhomogeneous magnetic fields, can attain masses as high as 15,000 daltons at full accelerating voltage and hence full sensitivity. New detectors for these high-mass ions have also been developed. Data systems can be used at these high masses, but the problems of calibration, mass defect (often greater than one nominal mass for very large ions) and digitization rate have to be overcome. Older data systems may not be adaptable to work at very high masses without both software and hardware modification.

C. MATRIX LIQUIDS

Glycerol, the most popular matrix liquid for bioorganic applications of FAB, is still the most popular starting point for choosing a matrix liquid. It is clear that even in cases where one might suspect that "protic" glycerol would react with the complex being studied, good spectra can be obtained in that matrix, e.g., hydrates and hydrogen-bonded solvates of tetraalkylammonium fluorides (*28*). In some cases, to clear up overlap caused by matrix ions, thioglycerol has been used. DMSO has been used as a matrix liquid (*29*), but we have found that many organometallic and coordination compounds are decomposed in it. Sulfolane is more promising, although it doesn't produce spectra that last as long. Another successful matrix liquid for coordination compounds and large macrocycle complexes is di-*tert*-amylphenol. Crown ethers, such as 18-crown-6, with 10% tetraglyme to depress the melting point, have given good results for organometallic compounds (*30*). We have recently found HMPA to give good results as a matrix liquid for fluoride systems, though its toxic nature makes one wary of its regular use. Poly(phenyl ether) and various other pump oils, including silicones, have been used with some success (*16*). Triton X100 has also been recommended as a solubilizing reagent (1%), though pure Triton X100 has been used for porphyrins (*16*). Doping the matrix liquid with a trace of acid or base often helps in obtaining positive- or negative-ion spectra. The addition of sodium or chloride salts can have the same effect. Many other viscous, relatively nonvolatile organic liquids have been tried. Neat liquid samples also work well if sufficient material is available, and slightly impure materials that give an oil rather than crystals can often serve as their own matrix. Do not hesitate to try new substances as matrix liquids appropriate to the nature of the compounds in which you are interested.

The study of various doping materials in a FAB matrix can, in fact, lead to the determination of chemical equilibrium constants as demonstrated by Caprioli (*31*) who was able to measure the pK_a values of a series of acids.

It is also possible to do the FAB experiment on solid materials without the presence of a matrix liquid. In such cases, the lifetime of the observed spectra is very much shorter but often adequate to characterize the material of interest. We have had considerable success with metal fluorides and metal fluorides coated on solid supports such as silica or alumina. The powdered sample is simply held on the probe tip with double-sided tape. This method can also be used for obtaining FAB spectra from unextracted TLC spots (*116*).

A new and promising matrix for less polar organometallics and coordination compounds is *p*-nitrophenyl octyl ether.

D. RELATION TO OTHER "SOFT" IONIZATION TECHNIQUES

As Campana has suggested (*14*), FAB and SIMS spectra are very similar in nature. This is perhaps in part due to the fact that the so-called fast-atom beam may well be a mixture of both ions and neutral particles (*32*). Since the deflection of the "low-energy" charged species in the ion gun does not remove the very energetic ions formed by the acceleration of multiply charged ions, they are then only partially neutralized by collision. It seems more a matter of nomenclature, with FAB sources being found on instruments designed as organic mass spectrometers, and SIMS being more likely on "surface science" instruments, often with quadrupole analyzers.

FAB is most often compared to the soft ionization method known as field desorption (FD) mass spectrometry, a technique in which the sample, deposited on an emitter wire coated with microcrystalline carbon needles, is desorbed under the influence of a high electric field gradient. As usual, bioorganic systems are best represented by both techniques (*21, 33*). Though FAB is the easier of the two, they are complementary, FAB being particularly suited for the case of extreme thermal lability and FD for the case of chemical lability or matrix interference. Cerny *et al.* (*33*) compare the two techniques for the study of coordination complexes and conclude FD is better for molecular-ion determination, while FAB provides better fragmentation information, which is useful in elucidating structures.

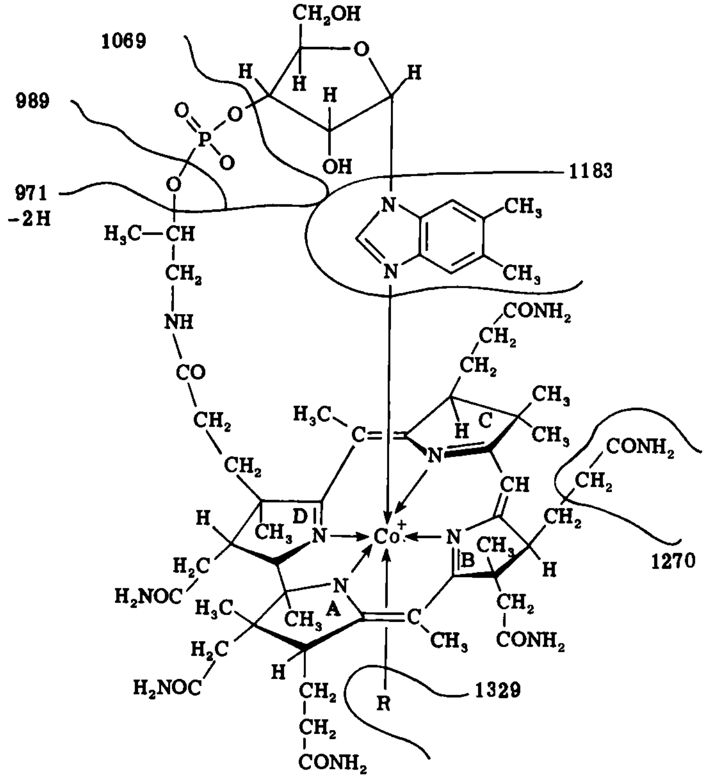
Laser desorption (LD) mass spectrometry is at an even less developed stage for organometallic and coordination compounds than is FAB (*19, 34–35*), though pure inorganic application preceded organic applications. Typically, pulsed lasers are used with time-of-flight (or quadrupole) mass analyzers. Thermal degradation seems to be greater than for other desorption methods. Similarly, plasma desorption (PD), or ^{252}Cf desorption, is based on the use of the californium fission fragments to energize and desorb samples from thin foils. Very high-molecular-weight species are detected (4000–10,000 daltons) using time-of-flight mass analyzers, which are, unfortunately, low resolution devices. It has been suggested (*34*) that all the desorption ionization techniques (DI) should be classed together and should include, in addition to the above, thermal desorption and electrohydrodynamic desorption, all being relatively "soft" and capable of yielding high-mass spectra.

III. Applications to Organometallic Compounds

Organometallic compounds were featured in the first published FAB paper by Barber *et al.* (*5*), and have been the subject of a brief review (*22*). Most exciting was the report that FAB yielded good spectra for vitamin B_{12} and its coenzyme. More details appeared in the proceedings of a conference held the previous year (*4*) and in a report in *Nature* (*8*). Prior to learning of these results, among others, we had also looked at vitamin B_{12} (*11*), using a Kratos demonstrator instrument (*10*). Most manufacturers offering FAB retrofits used vitamin B_{12} spectra in their promotional literature.

Barber's report on the FAB spectra of cobalamins is the most complete (*36*). The basic cobalamin structure is shown in Fig. 2, with the molecular weight ranging from 1343 to 1578 depending on the axial ligand R. In all cases, a reasonably intense quasi-molecular ion (i.e., M + 1), is observed in the positive-ion spectra obtained from a glycerol matrix, with an intense peak at *m/z* 1329, corresponding to the loss of the axial ligand, CN, CH_3, the coenzyme side chain, or OH. They reported the relative intensities of the M + 1 peak as $1355 > 1344 > 1579 > 1346$. Major losses then occur from the 1329 peak, as illustrated on Fig. 2. Although some acetamide is lost, major fragmentation occurs from the other axial chain. Dimethylbenzimidazole is lost, followed by the sugar and phosphate, yielding the base peak at *m/z* 971. The negative-ion spectra show M − H ions as well as ions for the attachment of a chloride ion [e]. These spectra are relatively clean, long-lasting, and free from thermal decomposition.

McLafferty *et al.* (*37*) studied the collisionally activated dissociation (CAD) of the ions resulting from the fast-atom bombardment ionization of cyano- and methylcobalamins, using a tandem mass spectrometer. They showed that *m/z* 1329 is produced only from the quasi-molecular ion. Similar CAD spectra are produced by both the quasi-molecular ions and the 1329 peak, indicating that essentially all fragmentation arises from this latter ion. CAD spectra produced for the 1329 ion derived from methylcobalamin or vitamin B_{12} coenzyme are also similar. This is consistent with the work of Taylor (*10*), who used linked-scan metastable ion techniques in a conventional double-focusing mass spectrometer to show the same thing. The sequential



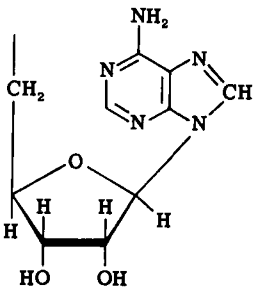
	R	Mol. wt.
Cyanocobalamin	CN	1354 + 1
Methylcobalamin	CH_3	1343 + 1
Hydroxocobalamin	OH	1345 + 1
Coenzyme B_{12}		1578 + 1

FIG. 2. Vitamin B_{12} FAB–MS fragmentation. [Reproduced in part with permission (*36*).]

losses from the axial ligand suggested by Barber are verified by both the tandem MS (*37*) and linked-scan (*10*) studies, though McLafferty warned that if the structure of the vitamin were not already known, then alternate fragmentation of the parts of the molecule could cause confusion in the assignment of the structure.

Taylor (*10*) also showed that high resolution was possible with FAB and that it could be applied to ions as large as these vitamins. However, higher resolution at high masses becomes essential, not for empirical formula determination (which for metal containing systems is often done better by a fit to the isotopic abundance patterns), but simply to be sure of resolving nominal masses as the molecules studied get heavier.

Schwartz *et al.* (*38*) reported on the use of FAB for "unequivocal and rapid molecular weight determination of corrins," with two cyano groups as the axial ligands. They reported no M^+ or $(M + H)^+$ ions, but rather the loss of both axial CNs, corresponding to reduction of the metal from Co(III) to Co(I), analogous to the EI behavior. However, negative-ion spectra gave very strong $(M - H)^-$ ions ranging from 20 to 100% relative intensity. Field desorption MS of cobalamin derivatives has been compared to FAB (*39*) with the suggestion that, for the type of compound discussed above, FD gives ions characteristic of the thermal degradation process, while FAB produces ions more characteristic of impact-ionization processes. However, because only positive-ion FAB was employed in this latter study, they did not observe the negative-ion spectra of the essentially intact parent molecule less a hydrogen.

Meili and Seibl (*40*) have investigated matrix effects in the FAB analysis of cobalamins to determine if changing from a glycerol matrix would improve the chances of observing molecular ions for such systems, which so readily suffer cleavage of the axial ligands, as discussed above. For cobyrinic acid derivatives, they achieved promising results with the ethyl and butyl esters of citric acid (TEC, TBC), benzoic acid benzyl ester (bzbz), and 2-nitrophenyloctyl ether (NPOE), all of these providing information on one or both axial ligands. Ion intensities are $(M - 2CN)^+ > (M - CN)^+ > (M)^{+\cdot}$ (bzbz only). The $(M - CN)^+$ ion dominates the spectrum in NPOE. They suggest that the slightly oxidizing matrix prevents the metal valence change from Co(III) to Co(II). The abundance of the molecular ion versus $(M - 2CN)^+$ changes from 120–150% immediately after insertion to 20–30% after a few minutes. These results suggest that if any metal-containing system appears to give, as the highest mass ion in FAB, a species corresponding to the reduction of the metal, then a weakly oxidizing matrix such as NPOE

TABLE I

COMPARISON OF EI AND FAB DATA[a]

O			S	
EI	FAB	Ion$^+$	EI	FAB
0.3	—	M	0.1	—
—	0.4	(M + 2Gl − 2H)[b]	—	—
25.9	49.3	Ph_3Sn	25.5	56.6
3.5	1	Ph_2Sn	2.4	—
8.9	22	PhSn	9.9	24.0
8.4	6.5	Sn	7.9	13.3
—	3.2	(Sn + Gl − H)[b]	—	—
3.3	2.5	C_6F_5	—	5.9

[a] $(C_6H_5)_3SnEC_6F_5$, E = O, S.

[b] Gl, glycerol.

is advisable. One might similarly predict that in negative-ion spectra, where species appear to be undergoing unwanted oxidations, a reducing matrix should be considered.

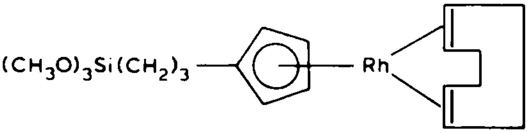
A. MAIN GROUP EXAMPLES

We have studied the FAB–MS of some phenyl derivatives of the Group IV elements (*41*). In Table I, a comparison of the EI and FAB (glycerol) spectra of $(C_6H_5)_3SnEC_6F_5$ (E = O or S) is made. Unfortunately, in this case FAB does not give a more intense molecular ion than does EI, though this might not be considered surprising since Group IV organometallics are known for their weak or absent parent ions. There is only slight evidence for complexation of the sample with the glycerol matrix.

Triphenylgermanium and tin and lead halides were examined in both glycerol and sulfolane matrices. In the case of sulfolane, ions were sometimes observed corresponding to the coordination of a sulfolane molecule to the organometallic halide, but simple parent ions were not seen. In contrast, Pang and Costello reported the FD spectra of some organogermanes with good molecular-ion intensities (*42*). In a rather different FAB use of Group IV organometallics, Wong *et al.* (*43*) reported on the use of a silicone pump fluid as the bombarding particle.

FAB and FD–MS have also been used for the determination of organoarsenicals such as arsenobetaine, $(CH_3)_3As^+CH_2COO^-$, in biological systems such as seafoods (*44, 45*). EI gives no molecular ion for this compound. The FD spectra showed decarboxylation–protonation to give $(CH_3)_4As^+$ (the base peak) as well as dimeric and trimeric species. Arsenocholine bromide was debrominated to give the base peak. Impurities in the marine extracts did, however, complicate the spectra. The FAB spectrum of arsenobetaine in glycerol was similar to the FD observations, with extra peaks to provide more structural information. In actual marine extracts, the quantities of arsenicals were so low that glycerol dominated the spectrum, but under high resolution conditions the protonated arsenobetaine at *m/z* 179.0053 ($AsC_5H_{12}O_2$) was measured with reference to the glycerol $(2M + H)^+$ ion, using a multichannel analyzer for signal averaging. Thus though the spectra of the real extracts were less clear than those from FD, in all cases with the long-lived spectra, high resolution permitted the detection of the arsenical in all samples examined.

Barber's group also investigated the application of FAB to transition-metal organometallics (*4, 8*). The silylcyclopentadiene–cyclooctadienerhodium compound (**I**) was both thermally labile and moisture



sensitive and gave no worthwhile mass spectrum, using other means of ionization. It was an oil, and its FAB spectrum was obtained as the neat liquid, without the use of a matrix liquid. The compound, being moisture sensitive, is likely to have reacted with glycerol. A strong parent ion was observed at *m/z* 438. The other important high-mass ions corresponded to the loss of neutral C_8H_4, trimethoxysilane, trimethoxysilylethylene, and the corresponding propylene. The rhodium COT bonds break readily, while rhodium remains strongly attached to the cyclopentadienyl fragment. Prominent silicon-containing positive ions also include $(CH_3O)_3Si^+$ and $(CH_3O)_2SiH^+$.

B. TRANSITION METAL EXAMPLES

They also looked at the spectra of ionic complexes such as $(Ph_3P)_4Au^+ClO_4^-$, which gave a simple positive-ion spectrum essentially corresponding to that of the cation and a successive loss of ligand. Loss of biphenyl was also observed. The negative-ion spectrum was that of the perchlorate anion.

Minard and Geoffroy (*30*) used 18-crown-6 (with 10% tetraglyme to depress the melting point) as their matrix liquid for organometallics to avoid the stability problems that glycerol or other protic solvents might have presented. They looked at two rhodium compounds, $(Ph_3P)_3RhCl$, i.e., Wilkinson's catalyst, and $C_8H_{12}Rh(PPh)(Cl)RhC_8H_{12}$, and a cobalt cluster compound, $(Ph_2P)_3—Co_3(CO)_6$. Molecular or overlapping molecular and quasi-molecular ions were observed. Successive loss of carbonyl was observed, just as would be expected from EI spectra.

Davis *et al.* (*46*) studied a series of organometallic complexes of rhodium, ruthenium, rhenium, palladium, and platinum, including metal cluster systems of iron and osmium. They used a series of matrix liquids including diamylphenol (DAP), glycerol, and carbowax 200. Wilkinson's catalyst gave similar results from the DAP to Minard's from a crown–glyme matrix. They show that FAB gives good spectra for triphenylphosphine complexes whose EI spectra are dominated by ions arising from the Ph_3P, produced by thermal decomposition of the complex. $ReCl(CO)_3[P(C_6H_4F\text{-}p)_3]_2$ and the corresponding ONO_2 compound having a *p*-methyl group in place of the *p*-F group both showed, as the highest-mass species, the ion $[(M + H)X]^+$. No evidence for the loss of X in solution has been reported. The Re—X bond may be particularly labile after ionization. These compounds did not give negative-ion spectra, suggesting that ionization occurs in the matrix, either via dissociation and loss of X or by protonation, to give a quasi-molecular ion, which may then fragment. The cluster compound $Fe_4(H)C(CO)_{12}AuPPh_3$ gave quasi-molecular ions in both positive- and negative-ion modes. The addition of a proton rather than its loss is unexpected in the negative mode. The salt $[Os_4H_3(CO)_{12}(MeCN)_2]PF_6$ gave both positive- and negative-ion spectra. The former gives the expected cation as the highest mass species, though the most intense ion corresponds to the additional loss of the acetonitriles. This latter ion is also seen in the negative-mode spectra, and it corresponds to species reported in the electrochemical reduction. Neither mode shows the ion pair of the parent molecule.

Sharp *et al.* (*47, 48*) used FAB–MS (with the crown–glyme matrix discussed above) to examine a series of rhodium, iridium, and platinum organometallic complexes containing either σ- or π-bonded cumulene ligands. For both rhodium and platinum compounds, the metal–bis(triphenylphosphine) cation is the base peak, while for iridium a similar ion is obtained, but with one carbonyl ligand remaining as well. Platinum complexes gave the most intense molecular ions (up to 35% relative intensity), while the rhodium molecular ions were least intense. Fragmentation occurred at the metal–ligand bond, the cumulene always being lost intact. The FAB spectra of rhodiumtris(triphenylphosphine) chloride, Wilkinson's catalyst, also reported by

Minard (*30*), and by Davis (*46*), who used a diamylphenol–acetonitrile matrix, did not show any parent molecular ion or quasi-molecular ion as the others had reported. $Ir[P(C_6H_5)_3]_2COCl$ (Vaska's compound), its corresponding rhodium derivative, and $Pt[(C_6H_5)_3]_2(C_2H_4)$ were also obtained for comparison. It is clear that greater intensities of high-mass fragments and molecular ions were observed when heavier bombarding particles were used. It is suggested that reproducibility between laboratories is equivalent to that for EI spectra. They also showed that isotopic cluster patterns are adequate to identify species without resorting to exact mass measurement. Sharp suggests that the Minard crown ether matrix will become the standard for organometallics.

Tkatchenko *et al.* (*49*) have compared the FAB and FD spectra of cationic η^3-allylic complexes of palladium and nickel. They found an intense cation and few fragments from FD data, while FAB is reported to give a smaller cation peak and numerous fragments. Since they used glycerol or glycerol–DMF matrices, they were perhaps not working under optimal conditions found by others such as Minard or Davis above. They were also able to observe species resulting from ligand exchange when they had two species present in the matrix liquid.

Kalinoski *et al.* (*50*) studied palladium-mediated reactions of organomercurials with glycals. If a heteroarylmercuric acetate, a chiral pyranoid or furanoid glycal, and palladium(II) acetate were added in equimolar quantities to a glycerol droplet, the FAB spectrum showed both the heteroarylpalladium species, formed by transmetallation from the mercurial, and the adduct formed by insertion of the glycal double bond into the palladium–heteroaryl carbon bond. Thus FAB has been used to observe labile organometallics not previously reported.

We can thus conclude that, though the applications of FAB to organometallics is still in its infancy, the technique shows great promise. It certainly works least well where EI works best, as we found for symmetrical nonpolar tetraaryls of Group IV elements. It obviously works best for those situations for which EI is of no value. In the intermediate case, there appears to be good evidence that FAB is complementary to FD. One will not replace the other, and at this stage it is difficult to say which will be the more successful in the long term, though FAB is easier to use.

IV. Applications to Coordination Compounds

We have studied some coordination compounds involving main-group Lewis acids (*51a*). In collaboration with Steve Hartman (*51b*) we have used FAB to detect the bis(quinuclidine)difluoroboron cation. The base peak in glycerol is the $D_2BF_2^+$ parent ion, with loss of quinuclidine giving the next most abundant ion. Group IV organometallic halides act as sufficiently strong Lewis acids to complex the glycerol or sulfolane matrix liquids, which are incorporated in some of the ions observed—sometimes displacing the halide. Triphenyltin bromide, for example, shows ions corresponding to coordination of sulfolane, as well as the corresponding ion that has lost either a phenyl group or bromine (*51*). We are not yet able to predict unequivocally the behavior of a weak Lewis acid when placed in a matrix liquid. There is clear evidence for ligand-exchange reactions in solution, and we are investigating the use of FAB as a complement to NMR for study of ligand-exchange reactions. Phosphonium salts, on the other hand, are somewhat more regular, showing the expected cation as well as weaker peaks for (cation)$_2$anion species. When we move to transition-metal complexes (*51*), the bistriphenylphospine–palladium halide system showed ions corresponding to one, two, three, and four halides.

Cerny *et al.* (*33*) have carried out extensive comparisons of FAB and FD mass spectrometry of neutral and 1+ and 2+ cationic transition-metal coordination complexes with glycerol used as the matrix liquid and with the sample solutions coated on aluminum foil to avoid memory effects. They concluded that FAB is preferable for the 1+ complexes, producing both parent ions and fragments. As one might have expected, FD gave better molecular-weight information on the neutral complexes, while FAB gave the fragments useful in elucidating structures. This may well be a case for further study of appropriate matrix liquids. Dicationic systems did not yield to either method, though some fragmentation information was obtained. Spectra were dominated by 1+ ions from reduction of the metal. They also found that for ligand losses and reductions, the FAB results paralleled the solution chemistry and thus could be useful in predicting solution chemistry. This would suggest that the observation of Meili and Seibl (*40*), that weakly oxidizing matrix liquids can prevent reduction of the metals, should receive wider attention. Among the metals included in the study by Bursey's group (*33*) were Re(III), Re(I), Ag(I), Rh(I), Os(II), Os(III), Os(VI), and Mo(VI). They also observed that in FAB, monodentate ligands are lost in preference to bidentate ligands, which are only lost from fragment ions. They report bipyridyl and phenanthroline-type ligands to be particularly tenaciously held. Fragments correspond either to reduction of the metal, or if that is an unfavorable process, by simple ligand loss. If there is a "redox accessible zero oxidation state," the redox process will be observed. For a series of Re complexes, they found chloride retained in preference to the π-acceptor ligand for Re(III), with the reverse observed for Re(I). Finally, they concluded that since the FAB and solution chemistries are so similar "that there is no evidence yet to discount a hypothesis that the energy-transfer process from the primary atom beam to the metal complex–glycerol matrix produces the initially formed parent ion in excited vibrational states of the ground state, which also can be populated by conventional thermolysis of the complex in a polar alcoholic solvent." In another work, the same group studied the FAB spectra of a series of copper complexes of biological interest (*52*).

Chan and Cook (*53*) studied the factors affecting the mass spectral sensitivity for ions sampled by field evaporation from a liquid matrix. These results, including those on metal complexes, show some of the types of interactions expected for ions in solutions, and they obtain results consistent with FAB–MS.

Barber's group has also compared positive- and negative-ion FAB and FD (*54*) for a series of iron(III) complexes, with hydroxamate-containing siderophores as the ligands. They propose these soft ionization techniques as a way to characterize siderophores (low molecular weight chelating agents with a high affinity for ferric iron, which are secreted by a wide range of microorganisms) and their metabolites. They found FD quite difficult, but useful results could be obtained with good technique. However, useful results were also obtained by FAB much more easily. FAB is recommended as the preliminary screening technique for potentially novel siderophores, with FD then being used to determine possible heterogeneity in the ferrichrome skeleton. Sensitivity was such that microgram quantities were adequate for identification of metabolites.

Johnstone *et al.* (*55, 56*) have extensively studied crown-ether complexes of metallic cations, using FAB. Metallic salts gave molecular ions of the type $[\text{crown} + M^{n+} + A^{(n-1)-}]^+$, where A is the anion. In particular, they looked at chlorides, acetates, and nitrates of Groups I and II, along with Cu, Hg, La, Ce, Th, Co, etc. They all gave molecular ions, but with a facility that reflected the complexation of the cations found in solution; e.g., $K > Cs > Na$ for 18-crown-6, other crowns giving different results. The method is proposed as being suitable for analyzing mixtures of metal cations in solutions at concentrations as low as 10^{-10} *M*.

They also proposed the method as a means of measuring stability constants for the complexes. As well, they analyzed the thermodynamics of the desorption process and were able to calculate the localized "temperature" which must be created in a small volume around the impacting fast atom for desorption of the complex to occur. Only species near the surface will be desorbed, since further into the bulk matrix excess translational energy is dissipated by multiple collisions. A temperature of about 860 K is calculated for the crown complexes, which compares to the 900 K reported by Stoll (*57*) for desorption from a heated filament of a benzo-15-crown-5–sodium ion complex. They again confirm that the best results for FAB are for preformed ions. Thus the matrix chemistry is critical for obtaining good spectra of neutral species. We have also (*51*) observed results similar to those of Johnstone for $HgCl_2$–18-crown-6 in a diamylphenol matrix. In glycerol, we saw the expected peaks for NaF–18-crown-6, except that weak peaks are also seen for a species with two crown molecules.

Kurlansik *et al.* (*58*) have used FAB to study disproportionation and recombination of synthetic porphyrin in the matrix. They observed reactions in the sample matrix that yielded new compounds from recombinations of molecular fragments, and if FAB is to be used extensively for peptide sequencing, warned of the importance of understanding these processes involving the formation and rupture of amides or peptide bonds. Bazzaz *et al.* (*59*) have used FAB to detect a new naturally occurring chlorophyll from a mutant maize plant. Glycerol did not yield a spectrum, but a mixture of chloroform and trigol as solvent and matrix gave molecular and quasi-molecular ions. However, "in beam" EI had to be used to determine the structure of the hydrocarbon tail. Leznoff and I (*60*) have successfully used DAP as a matrix for studying a series of synthetic porphyrins and their related metal complexes, including structures with two porphyrin rings and metals.

Barber *et al.* (*61*) have used FAB to study the antibiotics bleomycin A_2 and B_2 and their metal complexes. In particular, the ferrous sulfate complex of bleomycin A_2 shows a pseudomolecular ion at m/z 1566, corresponding to the salt ($A_2 - H^+ + FeSO_4$) since the amide hydrogen of the histidine residue is lost on complexation. An ion at m/z 472 corresponds to the ferrous ion complexed to the surrounding ligands but lacking the disaccharide groups and the peptide chain.

Another biomedical area of interest in metal complexes concerns various anticancer drugs. Puzo *et al.* (*117*) and Theodoropoulos (*63*) have used FAB to study cisplatin [i.e., *cis*-$Pt(NH_3)_2Cl_2$] and its complexes and related compounds. For the 1:2 complex with guanosine, peaks due to the complex less a Cl, or less Cl and HCl, along with their corresponding glycerol adducts were observed. Less clear results were observed for other amino acid complexes (*63*). Cohen *et al.* (*62*) and Costello *et al.* (*64*) have used FAB to study the complexes of technitium(III) and technitium(I) and -(V), respectively, these compounds being important radioactive materials for diagnostic imaging. Cohen favored monothioglycerol as the matrix agent. For monovalent cations of technitium(III), he obtained intense cation spectra and distinctive fragmentation information. Costello has identified the probable species present in some of the commercially available Tc imaging agents, using FAB with various mixed matrices involving glycerol. Hansen *et al.* (*65*) report FD to be more successful than FAB in identifying another Tc complex, pointing out the difficulty of predicting success of the method for any one type of compound.

V. Applications to Other Inorganic Systems

FAB has also been used for basic surface analysis of inorganic solids such as glasses (*66, 67*) and zeolites (*68, 69*). In this respect, the use of FAB closely parallels that of SIMS. Reproducible results are obtained, which can be quantified, while organic materials absorbed on the surfaces can also be determined. It also proved possible to use FAB to determine a depth-profile analysis of these samples. No charging effects, such as those that may cause difficulties with SIMS, were observed. Dwyer *et al.* (*68*), in their work on zeolites, correlate the surface Si^+/Al^+ ratio with the bulk Si/Al ratio and show the ion ratio to be dependent on the bulk atom ratio rather than on the zeolite structure. Negative-ion FAB studies were used to investigate the presence of paired aluminum species in both zeolites and aluminas (*69*). We have found that FAB is an ideal way of measuring the nature of inorganic or quaternary ammonium fluorides supported on alumina or silica, in particular where the presence or absence of bifluoride ion is important (*28, 51*). Coverdale *et al.* (*70*) have used negative-ion FAB to investigate the structure of rhenium(VII) oxide on alumina, and they obtained spectra similar to those of the bulk unsupported material. Similarly, supported NH_4ReO_4 shows quantitatively comparable spectra to be bulk crystalline material.

FAB–MS has been compared to the analytical use of negative-ion FD in the determination of fluoroborate anion in water at the ppb level (*71*). Positive FAB is however only sensitive down to the microgram level in glycerol and other matrix liquids, but negative FAB results were not reported. Smith (*72*) has reported the use of FAB for isotope-ratio analysis of such biologically important metals as calcium, magnesium, zinc, and iron. The long-term stability of spectra are an advantage in achieving statistically good results. Other researchers have evaluated the usefulness of adding inorganic salts, such as KCl, NaCl, or $AgClO_4$, to solutions of the analyte in glycerol (*73, 74*). Silver ion, in particular, adds an isotopic pattern to the spectra, which aids in picking out the ions of interest from a background that may well be very complex.

Javanaud and Eagles (*75*) have studied in detail the positive and negative FAB spectra of simple inorganic salts involving both various metal chlorides and sodium salts of some complex anions. They report that, in general, the FAB data more closely resemble FD rather that EI mass spectral data. Various polymeric species are also observed, as will be discussed below. Teeter (*76*) has similarly studied anionic surfactants and other sulfonate salts. The spectra were all relatively easy to interpret "knowing in advance the structures involved." He suggests that, for these systems, the application of FAB to quantitative analysis is not easy, with glycerol certainly complicating the spectra. Spectra were not additive with respect to the condensed phase. Teeter used a computer program, written for use on either a personal computer or a larger system, to work out all the possible combinations present.

We have looked at a simple inorganic material, stannous chloride, using positive and negative FAB in glycerol and in other matrix liquids (*41*). The negative-ion spectrum in HCl-doped glycerol showed ions corresponding to $SnCl_2$, $SnCl_3$, and $SnCl_3 \cdot H_2O$. The latter diminishes as HCl concentration increases, as does the $SnCl_2OH$ intensity. The base peak is the chloride ion, followed in intensity by the tin trichloride anion. Glycerol-containing ions were weak except for the chloride adduct. In the positive-ion spectrum, species such as $(SnCl)_2$, glycerol-H, and SnCl with one and two molecules of coordinated glycerol were observed.

The most extensively studied of the simple inorganic systems have been the alkali metal halides (*75, 77–80*). KI and CsI have been used as calibration compounds for high-molecular-weight studies, since clusters of the type M_nX_{n-1} are readily observed in the positive-ion spectra with n values of 50 or higher [values greater than 200 are now observed, i.e., masses exceeding $m/z = 50{,}000$ (*79, 80*)] being reported. Campana and co-workers have shown that there are two major reaction pathways for decomposition of the cluster cations, involving losses of either MX or of $(MX)_2$. In the negative-ion spectra, the corresponding anions contain an extra halide rather than the extra metal cation, but the behavior is otherwise the same. Interestingly, the intensity of the cluster species does not fall off regularly with n. Rather the data show regions of extra stability, and hence spectral enhancement, centered on $n = 13$, 22, and corresponding regions of low abundance for clusters having n greater than the stable points by one or two. Collisionally activated successive reactions of these clusters have also been reported (*75, 81*). Campana also reports (*80*) that "these extended mass spectra are fit to the distributions predicted by a model based on random bond breaking . . . when Bethe lattices of the appropriate coordination number are used," i.e., these clusters from solution mimic the solid state structure. We (*51*) have looked at the corresponding glycerol–MF systems, which have as an additional factor the possibility of strong H bonding between the fluoride ion and the OH proton of the matrix. Clusters are observed, which are similar to those seen for the other alkali metal halides, but complexation with the glycerol is more common until very high MF concentrations are reached, i.e., in the region of a 1 : 1 mol ratio. Most astonishing, however, is the observation in the positive-ion spectrum of a weak series of glycerol · $(MF_nF^+$. At first glance one might attribute this behavior to the presence of the bifluoride ion. However, this is ruled out by the negative-ion spectrum, which is dominated by the simple fluoride ion with no evidence for bifluoride. Bifluoride is seen in systems intentionally doped with HF_2^-, or simply with water, leading to its formation. This we take to be the first example of a mass spectrum of a strong H bond to fluoride.

VI. Applications of Secondary Ion Mass Spectrometry

A complete review of the inorganic and related applications of SIMS is beyond the scope of this article, since the technique is so much more mature than FAB, although for a long time it has been confined chiefly to surface chemistry studies. It is only with the development of the liquid-matrix technique that "organic" SIMS became popular. However, there are a great many similarities between the two techniques, and as mentioned earlier, SIMS experts feel that the FAB workers are basically "reinventing the wheel." Although this may be the case, and the similarities between the two techniques are great, the availability of FAB on the organic mass spectrometers available to most inorganic, organometallic, and coordination chemists has resulted in a burgeoning of interest. Typical of the recent reviews of SIMS is the work of Winograd (*17, 82*). We shall mention briefly some of the SIMS work that closely parallels the FAB results described above.

The applications of SIMS to organometallic and coordination compounds have been pioneered by Cooks and Walton and their co-workers (*83–90*). They have used solid matrices, such as ammonium or sodium chlorides, to decrease the abundance of ions resulting from intermolecular processes while increasing the abundance of ions that are structurally informative. Their results on triphenyltin chloride (*83*) are very similar to our FAB results. Interestingly, they report that neither iron nor manganese trisacac gives a parent ion in SIMS, while weak ones are observed in simple EI spectra. They also report on the similarity of SIMS to laser microprobe mass analysis (LAMMA) and the distinctions between them and EI. In a study of metal complexes of β-diketones (*84*), bimetallic species, such as $Co_2(acac)_4^+$ and the corresponding trisacac cation, are reported. These have, however, been reported in the past for EI spectra as well (*91*). In an approach that is the opposite to the derivatization used in EIMS (i.e., the production of volatile derivatives from polar or ionic species), Cooks (*85*) has reported the derivatization of neutral samples to produce nonvolatile ionic species via Bronsted or Lewis acids or bases, which enhance the sensitivity of the SIMS technique. Other work from these groups includes the study of silver complexes (*86*), nitrosylisocyanide complexes of chromium and molybdenum (*87*), the distinction between phosphines and phosphonium ions (*88*), the characterization of nickel complexes on oxide supports (*89*), and a study of phosphonium salts (*90*).

Another area of SIMS that has received a great deal of attention is the study of simple inorganic salts. Marien and De Pauw (*92*) have looked at the ion-beam-induced effects in SIMS spectra. It is clear that under high ion fluxes significant damage to the surface occurs, with the resulting complication of the spectrum. FAB, or liquid-matrix SIMS, is free of this effect but has the equivalent complication of reactions with the matrix, as discussed previously.

Campana's group has pioneered the development of high-performance SIMS instrumentation (*93*), in particular for studies at very high masses. They have investigated metal salt clusters in a manner analogous to the FAB results described in the previous section (*94–100*). For cubic-like structures, the CsI spectrum shows stable structures for species of the type $[Cs(CsI)_n]^+$ where $n = 13, 22, 31, 37, 52$, and 62 (*94*) with results now surpassing $n = 100$ (*95*).

Other examples of SIMS for surface analyses are studies of Cu_2S–CdS solar-cell samples (*101*) and the study of chemisorbed species on inorganic substrates such as methanol on Cu (*100*) and titania (*102*). De Pauw's studies of such adsorbed systems may prove to be valuable in determining the mechanism of catalytic reactions on surfaces (*103*). Winograd and co-workers (*104–6*) have studied chemisorption on metal surfaces, using SIMS. In a related study (*107*), Unger *et al.* have used molecular SIMS to study the reactions of thiophene on a silver surface. They observed the self-hydrogenation of thiophene on the surface of silver foils. Such studies are beginning to appear from the groups working with FAB sources.

VII. Applications of Other Related Techniques

Among the other "soft" ionization techniques is laser microprobe mass spectrometry (LAMMA) in which a laser pulse is used to vaporize a small amount of sample, as discussed in a 1982 review (*108*). Of interest to us is the application to the study of some cobalamins (*109*). (M + H) and (M − H) ions were observed in the positive and negative ion modes, respectively. However, there were few other high-mass fragments that could be used to impart structural information.

Schulten (*110, 111*) has used laser-assisted field desorption mass spectrometry to study some inorganic and organometallic systems. This method is intermediate between LAMMA and simple FD. Metal cations predominate from inorganic salts. The technique also showed clusters of the type reported from both FAB and SIMS studies. By carefully controlling the laser, a chlorophyll molecular ion could be obtained as well as fragments relating to its structure.

The most established of these other techniques is field desorption, but it has never been particularly widely used for inorganic, organometallic, or coordination compounds. In a 1982 review, Costello discussed in detail some of these applications (*108*)—note that only 16 references are quoted going back as far as 1972. She is the most active worker in the field having published papers on organogermanium, tin, and silicon compounds (*112*) and a technetate(V) complex used as a radiopharmaceutical (*113*). Staal *et al.* (*114*) have used FD to characterize various metal carbonyl 1,4-diazabutadiene compounds and report that in most cases only molecular ions are generated, though some loss of a single carbonyl is also observed. Since FAB is becoming more readily available than FD, is easier to use, and provides molecular weight and fragmentation information, though perhaps no less a "black art" than FD, it is unlikely that FD will establish as strong a position in the inorganic and related fields as will FAB.

The rarest of these specialized techniques, californium-252 plasma desorption mass spectrometry, has not been applied extensively to inorganic systems, though in a 1983 review (*115*) Macfarlane quotes several examples, such as polymeric "platinum blue," with molecular ions extending to *m/z* 3000. At present there are only 10 functioning systems and this certainly limits its growth.

VIII. Summary

In conclusion, I hope that I have shown that fast-atom bombardment mass spectrometry is a potentially useful tool for the synthetic chemist working in many areas of inorganic, organometallic, and coordination chemistry. In addition, as further fundamental research is done in the field with these applications in mind, the technique should become as routine as IR or NMR. Combined with developments in high-resolution NMR of solids, FAB should provide particularly useful data on supported catalytic reactions. Certainly FAB and the other complementary mass spectrometric techniques, mentioned in less detail, constitute a major way of quickly characterizing new compounds.

IX. Addendum

In the 5 months since this article was written, literature relevant to it has increased by one-third. At the end of the original 117 references I have added important new references, along with key words for each that will relate them to the text. They are presented topically in approximately the same order as material is discussed in the text, and I hope they will be of value.

REFERENCES

1. Miller, J. M., and Wilson, G. L., *Adv. Inorg. Chem. Radiochem.* **18,** 229 (1976).
2. Litzow, M. R., and Spalding, T. R., "Mass Spectrometry of Inorganic and Organometallic Compounds." Elsevier, Amsterdam, 1973.
3. Charalambous, J., ed., "Mass Spectrometry of Metal Compounds." Butterworths, London, 1975.
4. Barber, M., Bardoli, R. S., and Sedgwick, R. D., *in* "Soft Ionization Biological Mass Spectrometry" (H. R. Morris, ed.), p. 137. Heyden, London, 1981.
5. Barber, M., Bardoli, R. S., Sedgwick, R. D., and Tyler, A. N., *J. Chem. Soc. Chem. Commun.* 325, (1981).
6. Surman, D. J., and Vickerman, J. C., *J. Chem. Soc. Chem. Commun.* 324, (1982).
7. Williams, D. H., Bradley, C., Bojesen, G., Santikarn, S., and Taylor, L. C. E., *Am. Chem. Soc.* **103,** 5700 (1981).
8. Barber, M., Bordoli, R. S., Sedgwick, R. D., and Tyler, A. N., *Nature (London)* **293,** 270 (1981).
9. Taylor, L. C. E., *Ind. Res. Dev.* **124,** Sept. (1981).
10. Taylor, L. C. E., *Annu. Conf. Mass Spectrom. (ASMS), 29th, Minneapolis,* June (1981).
11. Miller, J. M., *ACS/CIC Symp. Bloomington,* June (1982).
12. Schulten, H. R., and Schiebel, H. M., *Naturwissenschaften* **65,** 223 (1978).

13. Martin, S. A., Costello, C. E., and Biemann, K., *Anal. Chem.* **54,** 2362 (1982).

14. Campana, J. E., *Int. J. Mass Spectrom. Ion Phys.* **51,** 133 (1983).

15. McNeal, C. J., *Anal. Chem.* **54,** 43A (1982).

16. Barber, M., Bardoli, R. S., Elliott, G. J., Sedgwick, R. D., and Tyler, A. N., *Anal. Chem.* **54,** 645A (1982).

17. Garrison, B. J., and Winograd, N., *Science* **216,** 805 (1982).

18. Rinehart, K. L., *Science* **218,** 254 (1982).

19. MacFarlane, R. D., *Acc. Chem. Res.* **15,** 268 (1982).

20. Fenselau, C., Cotter, R. J., Heller, D., and Yergey, J., *Int. J. Chromatogr.* **271,** 3 (1983).

21. Przybylski, M., and Fresenius, Z., *Anal. Chem.* **315,** 402 (1983).

22. Miller, J. M., *J. Organomet. Chem.* **249,** 299 (1983).

23. Stoll, R., Schade, U., Rollgen, F. W., Giessmann, U., and Barofsky, D. F., *Int. J. Mass Spectrom. Ion Phys.* **43,** 227 (1982).

24. Morris, H. R., Panico, M., and Haskins, N. J., *Int. J. Mass Spectrom. Ion Phys.* **26,** 363 (1983).

25. Franks, J., *Int. J. Mass Spectrom. Ion Phys.* **46** 343-6 (1983).

26. Rudat, N. A., and McEwen, C. N., *Int. J. Mass Spectrom. Ion Phys.* **26,** 351 (1983).

27. Hogg, A. M., *Int. J. Mass Spectrom. Ion Phys.* **49** 25 (1983).

28. Miller, J. M., and Clark, J. H., unpublished observations (1983).

29. De Pauw, E., *Anal. Chem.,* in press (1983).

30. Minard, R. D., and Geoffroy, G. L., *Abstr. Annu. Conf. Mass Spectrom. Allied Top., 30th, Honolulu* 321 (1982).

31. Caprioli, R. M., *Abstr. Conf. ASMS, 31st, Boston,* 69 (1983); *Analyt. Chem.* **55,** 2387 (1983).

32. Ligon, W. V., Jr., *Int. J. Mass Spectrom. Ion Phys.* 41, 205 (1982).

33. Cerny, R. L., Sullivan, B. P., Bursey, M. M., and Meyers, T. J., *Anal. Chem.* **55,** 1954 (1983).

34. Busch, K. L., and Cooks, R. G., *Science* **218,** 247 (1982).

35. Cotter, R. J., Van Breemen, R. N., Yergey, J., and Heller, D., *Int. J. Mass Spectrom. Ion Phys.* **46,** 395 (1983).

36. Barber, M., Bardoli, R. S., Sedgwick, R. D., and Tyler, A. N., *Biomed. Mass Spectrom.* **8,** 492 (1981).

37. Amster, I. J., Baldwin, M. A., Cheng, M. T., Proctor, C. J., and McLafferty, F. W., *J. Am. Chem. Soc.* **105,** 1054 (1983).

38. Schwartz, H., Eckart, K., and Taylor, L. C. E., *Org. Mass. Spectrom.* **17,** 459 (1982).

39. Schiebel, H. M., and Schulten, H.-R., *Biomed. Mass Spectrom.* **9,** 354 (1982).

40. Meili, J., and Seibl, J., *Annu. Conf. Mass Spectrom. (ASMS), 31st, Boston* May (1983).

41. Miller, J. M., *Int. Conf. Organomet. Coordi. Chem. Montreal* August, (1983).

42. Pang, H., and Costello, C. E., *Abstr. Conf. ASMS, 31st Boston* 379 (1983).

43. Wong, S. S., Stoll, R., and Rollgen, F. W., *Z. Naturforsch.* **37a,** 718 (1982).

44. van der Greef, J., and ten Noever de Brauw, M. C., *Int. J. Mass Spectrom. Ion Phys.* **46,** 379 (1983).

45. Luten, J. B., Riekwel-Booy, G., v.d. Greef, J., and ten Noever de Brauw, M. C., *Chemosphere* **12,** 131 (1983).

46. Davis, R., Groves, I. F., Durrant, J. L. A., Brooks, P., and Lewis, I., *J. Organomet. Chem.* **241,** C27 (1983).

47. Sharp, T. R., White, M. R., Davis, J. F., and Stang, P. J., *Abstr. Conf. ASMS, 31st, Boston* 371 (1983).

48. Sharp, T. R., White, M. R., Davis, J. F., and Stang, P. J., *Org. Mass Spectrom.* **19,** 107 (1984).

49. Tkatchenko, I., Neibecker, D., Fraisse, D., Gomez, F., and Farofsky, D. F., *Int. J. Mass Spectrom. Ion Phys.* **46,** 499 (1983).

50. Kalinoski, H. T., Hacksell, U., Barofsky, D. F., Barofsky, E., and Daves, G. D., Jr., personal communication.

51a. Miller, J. M., *Annu. Conf. Chem. Inst. Canada, Calgary* June (1983).

51b. Farquharson, M. J., and Hartman, J. S., *J. Chem. Soc. Chem. Commun.* (in press).

52. Cerny, R. L., Bursey, M. M., and Hass, J. R., *Abstr. Conf. ASMS, 31st, Boston* 369 (1983).

53. Chan, K. W. S., and Cook, K. D., *Anal. Chem.* **55,** 1306 (1983).

54. Dell, A., Hideer, R. C., Barber, M., Bordoli, R. S., Sedgwick, R. D., and Tayler, A. N., *Biomed. Mass Spectrom.* **9,** 158 (1982).

55. Johnstone, R. A. W., and Lewis, I. A. S., *Int. J. Mass Spectrom. Ion Phys.* **26,** 451 (1983).

56a. Johnstone, R. A. W., Lewis, I. A. S., and Rose, M. E., *Tetrahedron* **39,** 1597 (1983).

56b. Johnstone, R. A. W., and Rose, M. E., *J. Chem. Soc. Chem. Commun.* 1268 (1983).

57. Stoll, R., and Rollgen, F. W., *Org. Mass Spectrom.* **16,** 2296 (1981).

58. Kurlansik, L., Williams, T. J., Campana, J. E., Green, B. N., Anderson, L. W., and Strong, J. M., *Biochem. Biophys. Res. Commun.* April (1983).

59a. Bazzaz, M. B., Bradley, C. V., and Brereton, R. G., *Tetrahedron Lett.* **23,** 1121 (1982).

59b. Brereton, R. G., Bazzaz, M. B., Santikarn, S., and Williams, D. H., *Tetrahedron Lett.* **24,** 5775 (1983).

60. Miller, J. M., and Leznoff, C. C., unpublished observations.

61. Barber, M., Bardoli, R. S., Sedgwick, R. D., and Tyler, A. N., *Biochem. Biophys. Res. Commun.* **101,** 632 (1981).

62. Cohen, A. I., Glavan, K. A., and Kronauge, J. F., *Biomed. Mass Spectrom.* **10,** 287 (1983).

63. Theodoropoulos, D., Dalietos, D., Furst, A., Flessel, P., Guirguis, G., and Lee, T., *Abstr. ASMS Conf., 31st, Boston* 64 (1983).

64. Costello, C. E., Pang, H., Davidson, A., and Jones, A. G., *Conf. ASMS, 31st, Boston* 377 (1983).

65. Hansen, G., Heller, D., Yergey, J., Cotter, R. J., and Fenselau, C., *Chem. Biomed. Environ. Instrum.* **12,** 275 (1982–1983).

66. Surman, D. J., and Vickerman, J. C., *Appl. Surf. Sci.* **9,** 108 (1981).

67. Wakefield, C. J., Haselby, D., Taylor, L. C. E., and Evans, S., *Int. J. Mass Spectrom. Ion Phys.* **46,** 491 (1983).

68. Dwyer, J., Fitch, F. R., Qin, G., and Vickerman, J. C., *J. Phys. Chem.* **86,** 4574 (1982).

69. Dwyer, J., Elliott, I. S., Fitch, F. R., van den Berg, J. A., and Vickerman, J. C., *Zeolites* **3,** 97 (1983).

70. Coverdale, A. K., Dearing, P. F., and Ellison, A., *J. Chem. Soc. Chem. Commun.* 567 (1983).

71. van der Greef, J., Ten Noever de Brauw, M. C., Zwinselman, J. J., and Nibbering, N. M. M., *Biomed. Mass Spectrom.* **9,** 330 (1982).

72. Smith, D. L., *Abstr. Conf. ASMS, 31st, Boston* 248 (1983).

73. Allison, J., Musselman, B., Dolnikowski, G., and Watson, J., *Abstr. Conf. ASMS, 31st, Boston* 728 (1983).

74. Walther, H.-J., Parker, C. E., Harvan, D. J., Voyksner, R. D., Hernadez, O., Hagler, W. M., Hamilton, P. B., and Hass, J. R., *J. Agric. Food Chem.* **31,** 168 (1983).
75. Javanaud, C., and Eagles, J., *Org. Mass Spectrom.* **18,** 93 (1983).
76. Teeter, R. M., *ASMS Meet., Boston,* May (1983); and personal communication.
77. Taylor, L. C. E., Evans, S., and Wakefield, C. J., *ASMS Meet., Boston* May (1983).
78. Dunlap, B. I., Campana, J. E., Green, B. N., and Bateman, R. H., *J. Vac. Sci. Technol.,* in press (1983).
79. Campana, J. E., Coulton, R. J., Wyatt, J. R., Bateman, R. H., and Green, B. N., Submitted (1983).
80. Campana, J. E., and Dunlap, B. I., *Int. J. Mass Spectrom. Ion Proc.* **57,** 103 (1984); and Campana, J. E. Pittsburgh Conference, Atlantic City, March (1984).
81. Campana, J. E., Wyatt, J. R., Bateman, R. H., and Green, B. N., *Abstr. Conf. ASMS, 31st, Boston* 132 (1983); and Campana, J. E., and Green, B. N. *J. Am. Chem. Soc.* **106,** 531 (1984).
82. Winograd, N., *Prog. Solid State Chem.* **13,** 285 (1982).
83. Pierce, J., Busch, K. L., Walton, R. A., and Cooks, R. G., *J. Am. Chem. Soc.* **103,** 2583 (1981).
84. Pierce, J. L., Busch, K. L., Cooks, R. G., and Walton, R. A., *Inorg. Chem.* **21,** 2597 (1982).
85. Busch, K. L., Unger, S. E., Vincze, A., Cooks, R. G., and Keough, T., *J. Am. Chem. Soc.* **104,** 1507 (1982).
86. Pierce, J. L., Busch, K. L., Cooks, R. G., and Walton, R. A., *Inorg. Chem.* **22,** 2492 (1983).
87. Unger, S. E., Day, R. J., and Cooks, R. G., *Int. J. Mass Spectrom. Ion Phys.* **39,** 231 (1981).
88. Pierce, J. L., DeMarco, D., and Walton, R. A., *Inorg. Chem.* **22,** 9 (1983).
89. Pierce, J. L., and Walton, R. A., *J. Catal.* **81,** 375 (1983).
90. Ba-isa, A., Busch, K. L., Cooks, R. G., Vincze, A., and Granoth, I., *Tetrahedron* **39,** 591 (1983).
91. Miller, J. M., unpublished observations.
92. Marien, J., and De Pauw, E., *Int. J. Mass Spectrom. Ion Phys.* **43,** 233 (1982).
93. Colton, R. J., Campana, J. E., Bariak, T. M., DeCorpo, J. J., and Wyatt, J. R., *Rev. Sci. Instrum.* **51,** 1685 (1980).
94. Colton, R. J., Bariak, T. M., Wyatt, J. R., DeCorpo, J. J., and Campana, J. E., *J. Vac. Sci. Technol.* **20,** 421 (1982).
95. Barlak, T. M., Campana, J. E., Wyatt, J. R., Dunlap, B. I., and Colton, R. J., *Int. J. Mass Spectrom. Ion Phys.* **46,** 523 (1983).
96. Barlak, T. M., Campana, J. E., Wyatt, J. R., and Colton, R. J., *J. Phys. Chem.,* in press (1983).
97. Barlak, T. M., Campana, J. E., Colton, R. J., DeCorpo, J. J., and Wyatt, J. R., *J. Phys. Chem.* **85,** 3840 (1981).
98. Barlak, T. M., Wyatt, J. R., Colton, R. J., DeCorpo, J. J., and Campana, J. E., *J. Am. Chem. Soc.* **104,** 1212 (1982).
99. Barlak, T. M., Wyatt, J. R., Colton, R. J., DeCorpo, J. J., and Campana, J. E., *J. Am. Chem. Soc.* **104,** 1212 (1982).
100. Barlak, T. M., Campana, J. E., Colton, R. J., DeCorpo, J. J., and Wyatt, J. R., *J. Phys. Chem.* **85,** 3840 (1981).
101. Satkiewicz, F. G., and Charles, H. K., *Annu. Conf. Mass Spectrom., 29th, San Diego* 307 (1976).

102. Marien, J., De Pauw, E., and Pelzer, G., personal communication from E. De Pauw (1983).

103. De Pauw, E., and Marien, J., *Int. J. Mass Spectrom. Ion Phys.* **46,** 519 (1983).

104. Kimock, F. M., Baxter, J. P., and Winograd, N., *Surf. Sci.* **124,** L41 (1983).

105. Moon, D. W., and Winograd, N., personal communication (1983).

106. Moon, D. W., Bleiler, R. J., Karwacki, E. J., and Winograd, N., personal communication.

107. Unger, S. E., Cooks, R. G., Steinmetz, B. J., and Delgass, W. N., *Surf. Sci.* **116,** L211 (1982).

108. Costello, C. E., *Spectra* **8,** 28 (1982).

109. Graham, S. W., Dowd, P., and Hercules, D. M., *Anal. Chem.* **54,** 649 (1982).

110. Schulten, H.-R., Monkhouse, P. B., and Muller, R., *Anal. Chem.* **54,** 654 (1982).

111. Schulten, H.-R., Mueller, R., Haaks, D., and Fresenius, Z. *Anal. Chem.* **304,** 15 (1980).

112. Pang, H., and Costello, C. E., personal communication (1983).

113. Jones, A. G., Davison, A., LaTegola, M. R., Brodack, J. W., Orvig, C., Sohn, M., Toothaker, A. K., Lock, C. J. L., Franklin, K. J., Costello, C. E., Carr, S. A., Biemann, K., and Kaplan, M. L., *J. Nucl. Med.* **23,** 801 (1982).

114. Staal, L. H., Van Koten, G., Fokkens, R. H., and Nibbering, N. M. M., *Inorg. Chim. Acta* **50,** 205 (1981).

115. Macfarlane, R. D., *Anal. Chem.* **55,** 1248A (1983).

116. Chang, T. T., Lay, Jr., J. O., and Francel, R. J., *Anal. Chem.* **56,** 109 (1984).

117. Puzo, G., Prome, J. C., Macquet, J. P., and Lewis, I. A. S., *Biomed. Mass Spectrom.* **9,** 552 (1982).

118. Rollgen, F. W., and Giessmann, U., *Int. J. Mass Spectrom. Ion Proc.* **56,** 229 (1984).

FAB METHODOLOGY

Mahoney, J., Perel, J., and Taylor, S., *Am. Lab.* 92, March (1984).

Ross, M. M., Wyatt, J. R., Colton, R. J., and Campana, J. E., *Int. J. Mass Spectrom. Ion Proc.* **54,** 237 (1983).

Cook, K. D., and Chan, K. W. S., *Int. J. Mass Spectrom. Ion Proc.* **54,** 135 (1983).

Clay, K. L., Wahlin, L., and Murphy, R. C., *Biomed. Mass Spectrom.* **10,** 489 (1983).

Beckner, C. F., and Caprioli, R. M., *Biomed. Mass Spectrom.* 11, 60 (1984).

Musselman, B. D., and Watson, J. T., *ASMS Meet., San Antonio, Texas,* May (1984).

ORGANOMETALLICS BY FAB

Grotjahn, L., Koppenhagen, V. B., and Ernst, L., *Z. Naturforsch.* **39b,** 248 (1984).

Livingston, D. A., Pfaltz, A., Schreiber, J., Eschenmoser, A., Ankel-Fuchs, D., Moll, J., Jaenchen, R., and Thauer, R. K., *Helv. Chim. Acta* **67,** 334 (1984).

Gregory, B., Jablonski, C. R., and Wang, Y-P., *J. Organomet. Chem.* **269,** 75 (1984).

Tolun, E., Proctor, C. J., Todd, J. F. J., Walshe, J. M. A., and Connor, J. A., *Org. Mass Spectrom.* **19,** 294 (1984).

Tolun, E., Proctor, C. J., Heaton, B. T., and Todd, J. F. J., 13th *Br. Mass Spectrom. Symp.* (1983).

COORDINATION COMPOUNDS BY FAB

Unger, S. E., *Anal. Chem.* **56,** 363 (1984).

Costello, C. E., Brodack, J. W., Jones, A. G., Davison, A., Johnson, D. L., Kasina, S., and Fritzberg, A. R., *J. Nucl. Med.* **24,** 353 (1983).

OTHER APPLICATIONS OF FAB

Baldwin, M. A., Proctor, C. J., Amster, I. J., and McLafferty, F. W., *Int. J. Mass Spectrom. Ion Proc.* **54,** 97 (1983).

Smith, D. L., *Anal. Chem.* **55,** 2391 (1983).

Lyon, P. A., Stebbings, W. L., Crow, F. W., Tomer, K. B., Lippstreu, D. L., and Gross, M. L., *Anal. Chem.* **56,** 8 (1984).

Dolnikowski, G. G., Watson, J. T., and Allison, J., *Anal. Chem.* **56,** 197 (1984).

SIMS

Cox, III, X. B., Linton, R. W., and Bursey, M. M., *Int. J. Mass Spectrom. Ion Proc.* **55,** 281 (1983/1984).

Suib, S. L., Coughlin, D. F., Otter, F. A., and Conopask, L. F., *J. Catal.* **84,** 410 (1983).

Long, J. V. P., and Hinton, R. W., *Int. J. Mass Spectrom. Ion Proc.* **55,** 307 (1983/1984).

Ramseyer, G. O., Brenna, J. T., Morrison, G. H., and Schwartz, R., *Anal. Chem.* **56,** 402 (1984).

Pimminger, M., Grasserbauer, M., Schroll, E., and Cerny, I., *Anal. Chem.* **56,** 407 (1984).

MISCELLANEOUS

Castro, M. E., and Russel, D. H., *Anal. Chem.* **56,** 578 (1984).

Schueler, B., Feigl, P. K. D., and Krueger, F. R., *Z. Naturforsch.* **38a,** 1078 (1983).

Michiels, E., and Gijbels, R., *Mikrochim. Acta* **III,** 277 (1983).

Chait, B. T., and Field, F. H., *J. Am. Chem. Soc.* **106,** 1931 (1984).

Blumenthal, T., Bruce, M. I., Shawataly, U. B., Green, B. N., and Lewis, I., *J. Organomet. Chem.* **269,** C10 (1984).

Lehmann, W. D., Kessler, M., and Konig, W. A. *Biomed. Mass Spectrom.* **11,** 217 (1984).