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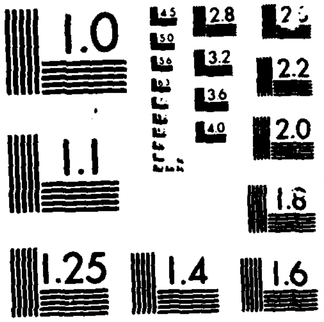

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SOME APPLICATIONS OF FAST ATOM BOMBARDMENT MASS SPECTROMETRY

by

J Hodson and A J Pidduck

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MATERIALS CENTRE

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SUMMARY

The fast atom bombardment (FAB) ionisation source for mass spectrometry (MS) is introduced, and the advantages over other ionisation techniques are discussed. Experimental factors are fully described. In initial work, FABMS is applied to the direct analysis of lubricant additives, thermally labile or involatile organic compounds such as macromolecules and ionic dyestuffs, and inorganic compounds. Applications published in the literature are reviewed. Attention is drawn to the high specificity of FABMS for surfactant species since these are often difficult to analyse by other methods.

1 INTRODUCTION

Fast atom bombardment (FAB)$^{(1)}$ provides a method for direct mass spectrometric (MS) analysis of condensed phases. FABMS has grown rapidly since its inception in 1981. It is now widely used to complement conventional electron impact (EI) and chemical ionisation (CI) organic MS techniques. The particular advantages of FABMS are:

(i) Good spectra are obtained from many thermally labile, involatile or ionic species. These are largely intractable using EI and CI methods.

(ii) Pseudomolecular and fragment ions are seen. Thus, as with CI, both molecular weight and structural information can be extracted from the mass spectrum.

(iii) Intense and long-lived spectra are obtained, especially when the sample is dispersed in a viscous high boiling matrix, such as glycerol. This compares with the inherently transient spectra produced by alternative methods of ionisation from condensed phases, such as field desorption (FD) and laser desorption (LD)$^{(2)}$.

(iv) Surface charging does not occur. This effect limits the applicability of the analogous technique of secondary ion MS (SIMS), where a fast ion beam is incident on the specimen.

(v) FABMS is experimentally simple, rapid and robust. This contrasts with the difficulties in FDMS of emitter and sample preparation.

(vi) Addition of a fast atom gun is the only modification required for conventional magnetic sector or quadrupole spectrometers equipped with a suitable insertion probe.

(vii) It is compatible with modern methods of mixture analysis such as LC/MS or MS/MS. Reverse phase HPLC is often the preferred separation technique for polar and thermally labile species. FABMS can then be carried out directly from a "moving belt" interface. Linked scanning MS/MS needs stable generation of molecular or pseudomolecular ions, preferably free from fractionation effects. FABMS fulfils these criteria. FABMS can also be applied to direct analysis of TLC spots.

This paper reports the results obtained during two short applications periods spent at VG Analytical Ltd, Altrincham, and at AWRE Aldermaston. These were used to assess the applications of FABMS to chemical systems of interest within DGDQA. The results are discussed in the context of available literature.

2 THE IONISATION PROCESS

2.1 Solids

Sputtering and ionisation processes which occur on impact of "fast" neutral particles, such as Ar, Kr or Xe of 4 to 10 keV energy, are the same as those known to occur under ion bombardment, as in the established surface analysis technique SIMS$^{(3,4)}$. Secondary ion emission following impact of a fast heavy particle against a solid surface is shown schematically in Figure 1. Figure 1(a) illustrates how the kinetic energy of the incident particle is lost to the solid in a collisional cascade process. Some of the particles in the tail of this cascade gain sufficient translational energy in a direction normal to the surface to be sputtered. In ionic solids, charge separation occurs and so particles can be directly sputtered as ions. In neutral solids, a proportion of particles can become ionised as they pass through the surface electric fields, though the majority of sputtered species are neutral. Figure 1(b) shows that a dense gaseous plasma of translationally excited particles, known as the selvedge, is formed before sputtering is complete.

In organic solids, ion-molecule reactions such as attachment or proton transfer, can occur within the selvedge, leading to pseudomolecular ions. Typical are $[M-H]^-$ and $[M+H, Na\ or\ K]^+$. Cluster ions, such as $[nM+H]^+$, can also occur. Electron transfer, leading to $M^{+\cdot}$ or $M^{-\cdot}$, is rare, unless M has a low ionisation potential or high electron affinity. Unimolecular ion decompositions occur, both within and outside the selvedge, giving rise to fragment ions.

Intense pseudomolecular ions are often observed, even from compounds which are thermally labile in their bulk state. This suggests that sputtering, by rupture of intermolecular bonds, occurs on a shorter timescale than is needed for the development of molecular vibrations ($<10^{-13}$ s). This phenomenon, which can be viewed as an extremely rapid local heating, is common to FABMS, molecular SIMS, ^{252}Cf "plasma desorption" and laser desorption(5). Thus similar mass spectra are often obtained from all these surface ionisation techniques.

2.2 Liquids

Liquids, so long as they are sufficiently involatile to prevent fast evaporation under high vacuum conditions, appear to behave similarly to solids. In FABMS, a viscous, high-boiling liquid such as glycerol is commonly used to disperse the sample. Optimum sensitivity is obtained from surface active species. Viscous flow presents a constantly replenished surface, leading to long-lived spectra. Barber et. at.(6) have used surfactant/glycerol systems to study the ionisation mechanism and aspects of quantitation. The general form of their results are shown in Figure 2, and the implications are summarised below:

(i) At low surfactant concentrations, before any coherent monolayer is formed, the relative signals from matrix and surfactant reflect their proportion in the bulk.

(ii) At high surfactant concentrations, signals from the matrix are completely masked. Thus no quantitation is possible when the concentration exceeds that critical for dense packed micelle formation.

(iii) Sputtering of pre-existing ions is a much more efficient process than ionisation processes occurring within the selvedge.

3 EXPERIMENTAL FACTORS

The experimental conditions used for this work are given in Table 1.

TABLE 1

	VG Analytical	AWRE
Atom beam	Xe	Ar
Energy (keV)	6	9
Ion-equivalent current (μA)	(Not measured)	10
Spectrometer	VG 7070E	Kratos MS50
Data System	VG 11/250	(UV output)
m/z range (u)	90-1400	20-1000

Liquid samples were coated directly on to the copper or stainless steel target. Solids were dissolved or dispersed in a drop of glycerol, or other matrix, and placed on the target surface. The target was approximately 3 mm × 5 mm in area, and mounted at the tip of a modified FD insertion probe. A typical analysis time was under 5 minutes.

Other experimental variables are now considered more generally in the following:

3.1 Source(1,7)

With a fast atom source there is no surface charging, so stable secondary ion spectra can be obtained from non-conductors. Potentials used for incident beam acceleration are independent of the ion extraction potential (accelerating voltage). Atom beams can be generated from ions contained within a saddle field(1). Charge transfer for instance, can occur by resonant exchange with atoms of the same type, or by capture of thermalised electrons.

Many workers have reported that their spectra are insensitive to ion content of the incident beam(7). Thus it is now common to use atom guns containing a high component of ions. Ion guns can be made more efficient, smaller and cheaper than atom guns, and can be source-mounted. Ion beams are necessary where direction focussing is required, as in surface SIMS imaging.

3.2 Target and Atom Beam(8,9)

Sputtering efficiency is proportional to the momentum of incident particles. Thus heavier noble gas atoms yield more intense FAB spectra. Xe is often preferred to Ar for this reason, despite its much greater expense. Atom energy (between 2 and 10 keV) has only a secondary effect on the degree of fragmentation present in spectra. The target material, which can be copper, stainless steel or polyimide, does not affect spectral form. However, choice of target does affect the ease with which liquid wetting takes place.

3.3 Geometry(9)

Maximum sensitivity is attained with the incident beam at 60° and the extracted beam normal to the sample surface. The plane of the sample should be arranged so that gravity acts to restore the liquid surface, since migration can occur under the pressure impact of the incident beam.

3.4 Matrix

Unless the matrix itself is of interest, optimum FAB spectra are obtained from sample species which are active at the matrix-vacuum interface. High boiling liquid matrices are needed. Viscosity must not be too high, and can be controlled by adjusting probe temperature. FAB matrices in common use are glycerol, monothioglycerol, tetraethylene glycol and diamylphenol. Additives which have been used to enhance solubility or ionisation are water, methanol, acetic acid, hydrochloric acid, sodium chloride, sodium hydroxide, ammonium chloride, dimethyl sulphoxide and NNN'N'-tetramethyl-1,4-benzenediamine.

3.5 Analyser

Fast atom sources are equally suited to use with magnetic sector and quadrupole analysers. However, the energy of sputtered ions covers a wide range, and so double-focussing is needed for acceptable resolution in sector instruments.

3.6 Mass Calibration

Compounds giving a series of marker ions extending to high masses are needed. Glycerol itself gives a useful series of cluster ions in both +ve and -ve ion modes. Certain alkali metal halide salts give regularly spaced cluster ions extending to m/z 10,000(10).

Accurate mass measurement requires simultaneous recording of sample and marker spectra at medium or high resolution. Using either a matrix-compatible surfactant as internal calibrant, or a movable split target with calibrant occupying one half, mass accuracies of within 10 ppm have been achieved(11).

3.7 Structure Identification

Most fragment ions in FABMS are unimolecular decomposition products from pseudomolecular ions. Thus the spectra are CI-like, and often more readily correlated with structure than spectra obtained with EI(2), where ion-radicals are the parent species.

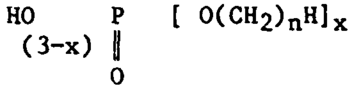
Linked scanning techniques can be applied, with or without collision induced dissociation (CID), to study fragmentation mechanisms in pure substances(2). These techniques can also be used to distinguish fragment ions from molecular ions. This is the basis of direct mixture analysis using MS/MS.

4 RESULTS AND DISCUSSION

4.1 Lubricant Systems

4.1.1 Gear Oil Additive

The +ve ion FABMS spectrum obtained directly from a proprietary anti-wear gear oil additive is shown in Figure 3(a). This additive has been characterised, by capillary GC/MS of the methylated derivative, as a mixture of alkyl phosphate esters of the form(12):

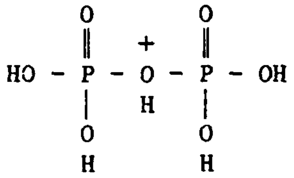


$$HO_{(3-x)}\overset{\displaystyle O}{\overset{\|}{P}}[O(CH_2)_nH]_x$$

where n = 8, 10, 12 ...

and x = mainly 1, 2

The FABMS spectrum is dominated by protonated molecular ions of these esters. It is similar in form to the molecular weight distribution suggested by GC/MS (Figure 3(b)), where methylation was necessary to avoid thermal degradation in the GC injector. Cluster ion series, starting at m/z 533 (323+210) and 645 (323+322), are also seen. A diphosphate ion occurs at m/z 179:



$$HO-\underset{OH}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-\overset{+}{\underset{H}{O}}-\underset{OH}{\overset{O}{\overset{\|}{\underset{|}{P}}}}-OH$$

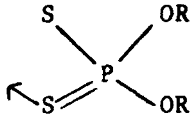
High sample acidity (pH = 1), implying preexisting +ve ions, is responsible for the intensity of the +ve ion spectrum. The -ve ion spectrum, and the positive ion spectrum of the methylated derivative were, by contrast, much weaker and contained many fragment ions.

4.1.2 Zinc Dialkyldithiophosphates (ZDDPs)

ZDDPs are important multi-role additives used in lubricants. FABMS spectra of propyl, n-pentyl and 2-ethylhexyl derivatives were obtained, either directly (if liquid) or in glycerol (if solid). The +ve ion spectra were intense and complex, showing two groups of isotopic cluster ions at m/z > molecular mass. The isotopic patterns are complex because Zn has 3 major naturally occurring isotopes [^{64}Zn (49%), ^{66}Zn (28%) and ^{68}Zn (19%)] and S has two [^{32}S (95%) and ^{34}S (4%)], separated by 2 u in each case. The highest mass cluster from each of the two cluster groups are assigned in Table 2. The spectrum of the pentyl ZDDP derivative is shown in Figure 4.

TABLE 2

HIGH MASS CLUSTER IONS IN +ve ION FAB SPECTRA OF ZDDPS

ZDDP Structure Zn L_2 where L =  , R = C_n- alkyl

n	MW (u)	L (u)	MASS OF CLUSTER (u) (m/z of lowest mass ion in isotopic distribution) Lower Mass Group	 Higher Mass Group
3	490	213	719 735 $\underline{751}$ 767	815 $\underline{831}$ 847 863
5	602	269	921 $\underline{937}$	1001 1017 $\underline{1033}$
8	770	353	1156 1172 $\underline{1188}$	1268 $\underline{1284}$
Assignment of ion structure: (where x = 0, 1 or 2)			$^{64}[Zn_2L_3H_x]^+$	$^{64}[Zn_3L_3SH_x]^+$

Note: Underlining denotes dominant cluster in each group.

The assignments in Table 2 are based only on correlations with differences in alkyl chain length, and on analysis of isotopic distribution (see Figure 4), and are to be regarded as tentative. The separation of clusters by 16 u suggests that ^{16}O and ^{32}S atoms become scrambled during the complex ion-molecule reactions which must be occurring.

Cluster ions are also seen in heated probe - EI mass spectra of certain metal carboxylates(13), where $M_4(OCOR)_6O$ is often the parent vapour-phase species. In fact, $Zn_3(OCOCH_3)_3O^+$ is an important ion in spectra from zinc acetate dihydrate. However, no cluster ions are observed in probe -EI spectra of ZDDPs(14), and few ions in the FAB spectra are coincident with those in the EI spectra.

Negative ion data were collected only in the case of pentyl ZDDP. A weak signal at m/z 270, characteristic of the liquid (LH^-), was observed.

4.1.3 Hydrocarbon Base Oils

Liquid alkanes of low volatility give fairly good +ve ion FAB spectra, in which M^{+} is prominent (Figure 5(a))(1). Hydrocarbon reference base oils gave +ve ion spectra of the type shown in Figure 5(b).

Characteristically, there was a broad maximum near m/z 350 to 400 containing a high proportion of even mass ions. Many of these could be $M^{+\cdot}$ ions from long chain alkyl benzenes. The relative absence of alkane $M^{+\cdot}$ ions implies that the spectrum arises from species having a degree of surface activity. A high-sulphur reference base oil gave very similar, though weaker, spectra. No -ve ion signals were detected.

4.1.4 ZDDP Additive Packages

Proprietary ZDDP additive packages contain a few % of the ZDDP, along with other species, in a hydrocarbon base oil, Their +ve ion FABMS spectra were found to be of similar form and strength to those obtained from pure ZDDPs indicating a high surface concentration. In the example shown in Figure 6 the high mass cluster groups are most intense at m/z 965 ($^{64}Zn_3$) and 865 ($^{64}Zn_2$). Interpolating from Table 2 suggests a mean alkyl chain length of ca. 4.2. This is consistent with the disclosed origin of the ZDDP as from a mixture of C_4- and C_5- alcohols. Some of the lower mass ions, such as those near m/z 290, 390 and 450 u, may be a common feature of ZDDP spectra, and thus also useful for diagnostic purposes.

4.1.5 Synthetic Lubricants

Aliphatic diesters(15) and polyethers(16) give strong +ve ion FABMS spectra in their own right, and thus offer little scope for selective ionisation of species that are not surface active. For instance, Figure 7 shows the similarity between EI and FAB mass spectra of dioctyl sebacate containing a known mixture of antioxidant additives. The FABMS spectrum contains protonated species (eg m/z 113, 315) and cluster ions (eg m/z 427), though most ions are common to the 2 spectra. However, whilst EI spectra need to be accumulated during distillation from a direct insertion probe, the FAB spectrum is a single step analysis, and thus free from fractionation effects. The intense and stable FABMS spectra generated are thus ideally suited to mixture analysis using linked scanning techniques.

4.2 Macromolecules

4.2.1 Biopolymers

By far the largest single application of FABMS in the literature has been the molecular weight determination and sequencing of polypeptides (polyamides)(17). Polypeptides generally give intense pseudomolecular ions in both +ve and -ve ion modes when dispersed in glycerol. This is because proteins contain both acid and base functionality and denature at the surface of polar solvents. Molar masses up to 9383 u, from human proinsulin, have been measured. Fragment ion series have been used to characterise the peptide sequence. The stability of spectra have allowed linked scanning techniques to be applied, confirming that the majority of fragments arise from unimolecular decomposition of the pseudomolecular ion. Simple cleavage of peptide linkages occurs, sometimes accompanied by hydrogen transfer. Spectra from polysaccharides and nucleoside polyphosphates have also been obtained(18).

4.2.2 Resins and Liquid Polymers

As shown in Figure 8, polyglycols yield strong +ve ion spectra. These contain pseudomolecular ions, although fragmentation increases with increasing molecular weight.

For instance, polypropylene glycol of mean MW 750 gives only weak pseudomolecular ions, even after addition of sodium hydroxide to enhance ion formation. Cluster ions can also form, as shown by glycerol. Thus FABMS does not give precise molecular weight distributions, and in this respect is more limited than field desorption(15).

Polyester resins were also examined, but signals were only observed in one out of four cases. No FABMS signals were detected from a liquid epoxy polymer. This initial work suggested that viscosity, temperature and choice of solvent have to be optimised before useful spectra can be obtained.

4.2.3 Solid Polymers

Characteristic FABMS spectra have been obtained from a number of solid polymers(19) using very low primary beam densities (2 keV Ar particles; 10^{-8} A.cm^{-2} equivalent ion current). Even at these levels, where signal strengths are very low, significant attenuation due to beam damage was noted. This indicates that experimental parameters need to be optimised to obtain successful FAB spectra from polymers.

4.3 Other Organic Compounds

Good FABMS spectra have been obtained directly from TLC spots(21). The stationary phase was transferred to the probe tip using double sided tape. Spectra from separated organic material were obtained by elution into a drop of glycerol (or other solvent) added to the probe tip. Similarly, spectra have been directly obtained from polymeric additives by addition of a drop of glycerol to the polymer surface(20).

4.3.1 Explosives Chemicals

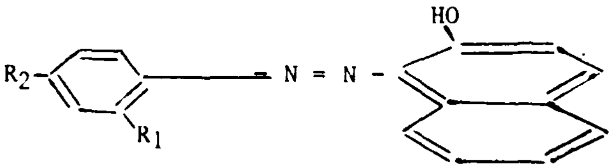
No FABMS spectra of explosives have been reported, though good spectra of several stabilisers have been obtained(15).

4.3.2 Surfactants

These are ideally suited to analysis by FABMS as discussed in section 2.4. FABMS spectra of many anionic, cationic and nonionic surfactants have been obtained and interpreted(22,23).

4.3.3 Organic Dyestuffs

Three azo dyes, of the general formula given below, were examined after dissolution in glycerol or diamylphenol.



Of these, only the ionic dye Acid Orange 7 (R_1 = H, R_2 = Na^+ SO_3-) gave FAB spectra, and these are shown in Figure 9. Strong pseudomolecular ions, and fragments resulting from azo cleavage(24) are seen. No +ve or -ve ion signals were detected from the non-ionic dyes Solvent Yellow 14 (R_1 = R_2 = H) or Hansa Scarlet RNC (R_1 = NO_2, R_2 = CH_3). A range of ionic (eg sulphonated) dyestuffs and their intermediates have been characterised using FABMS(24).

4.3.4 Organometallic Compounds

Many biochemicals of this type - such as porphyrins, vitamin B_{12} and chlorophyll - have been analysed successfully using FABMS(17). A Rhodium based catalyst complex also gave good spectra(1).

Metal carboxylates are common corrosion products(13). Figure 10 shows the +ve ion FAB spectrum of lead acetate trihydrate dissolved in glycerol. Solvent metal cluster ions dominate the spectrum, which contains little information on the anion. Similar effects were observed in spectra of zinc acetate dissolved in tetraethyleneglycol. Negative ion spectra, where examined, were very weak; Johnstone et. al (25) have found that a wide range of metal acetates, when dissolved in crown ethers, give +ve ion spectra dominated by an adduct ion of the form [crown ether + M^{n+} + L_{n-1}] where L = CH_3COO^-. This method thus allows easy characterisation of both anion and cation.

4.4 Inorganic Compounds

4.4.1 In Solution

A wide range of group I and II metal salts give strong +ve and -ve ion spectra after dissolution in glycerol(26). As in Figure 10, signals from the anion are weak in +ve ion spectra. However, in -ve ion spectra series of the type $[(CA)_n + A]^-$ are strong. Chlorides and nitrates of many metals dissolve in crown ethers to give -ve ion spectra of the type noted above for acetates(24).

4.4.2 Inorganic Solids

Strong and stable FABMS spectra were obtained from silica, iron oxide and zinc sulphide. These are shown in Figure 11. By contrast, virtually no signals were detected from zinc oxide or activated charcoal. Rudimentary surface information is obtained. Hence the observation of H-containing ions in Figure 11(b) and of Cl^- in Figure 11(d). In the literature, good spectra have been reported from stainless steel, rock minerals, pure metals and alkali metal halides(15). Metals and alkali halides yield many cluster ions. In the case of CsI, spectra extending to m/z 20,000 in both +ve and -ve ion modes have been recorded(19). Perturbations of an otherwise regular decay were interpreted in terms of geometrically unfavourable lattice structures. True surface studies can be made using low atom beam densities and ultra-high vacuum systems, and have been applied to the depth-profiling of a range of glasses(27).

5 CONCLUSIONS

5.1 Fast atom bombardment provides a method for obtaining mass spectra directly from involatile or thermally labile compounds. These are not tractable by conventional (EI or CI) MS techniques. Unlike FDMS, FABMS is experimentally simple and rapid.

5.2 This initial work has demonstrated that the introduction of the FABMS technique into our laboratories will extend the applicability of mass spectrometry to the following areas:

(i) Direct analysis of surface active agents, such as lubricant additives.

(ii) Analysis of thermally labile macromolecules including biopolymers.

(iii) Analysis of involatile organic compounds such as ionic dyestuffs.

(iv) Direct identification of TLC spots.

(v) Direct analysis of inorganic materials.

5.3 FAB spectra are often intense and stable, containing strong pseudomolecular ions. Optimum results are obtained when the compound of interest is dispersed at a viscous liquid surface, which underlines the high specificity of FABMS for surfactant species. This is of particular importance, since such compounds are often difficult to analyse by other means. However, careful consideration of the chemistry of the liquid surface and of the FAB ionisation process (which can produce cluster ions) is necessary for this application to be fully exploited.

5.4 Neutrals are the major sputtered species. Hence, higher sensitivity can be achieved if a secondary ionisation process is used in conjunction with FAB. Possibilities are tunable laser ionisation (Sputtered Atom Resonance Ionisation Spectral Analysis(28)) and chemical ionisation(29). Both methods give higher specificity in addition to increased sensitivity.

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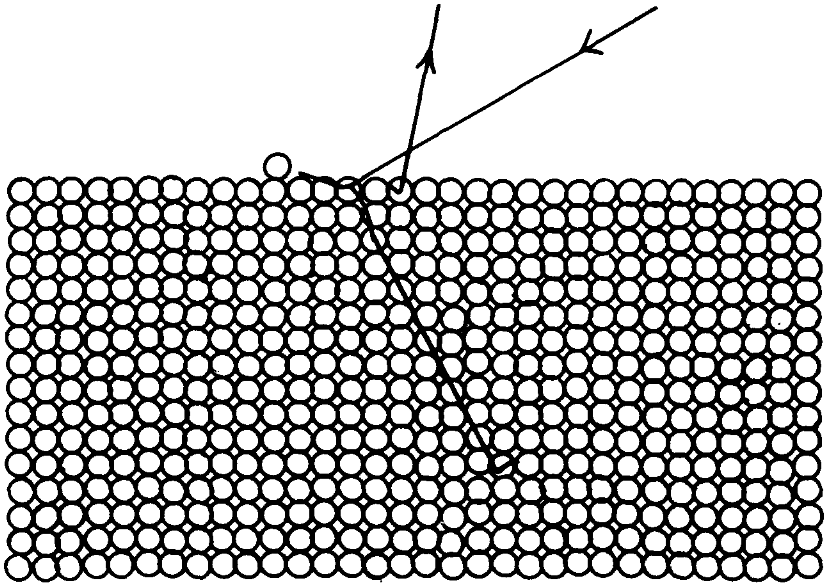
(a) Initial impact and collisional cascade (t = 0.0 ps; T_{local} = ambient)



(b) Selvedge formation (t = 0.4 ps; T_{local} ~ 1000K)

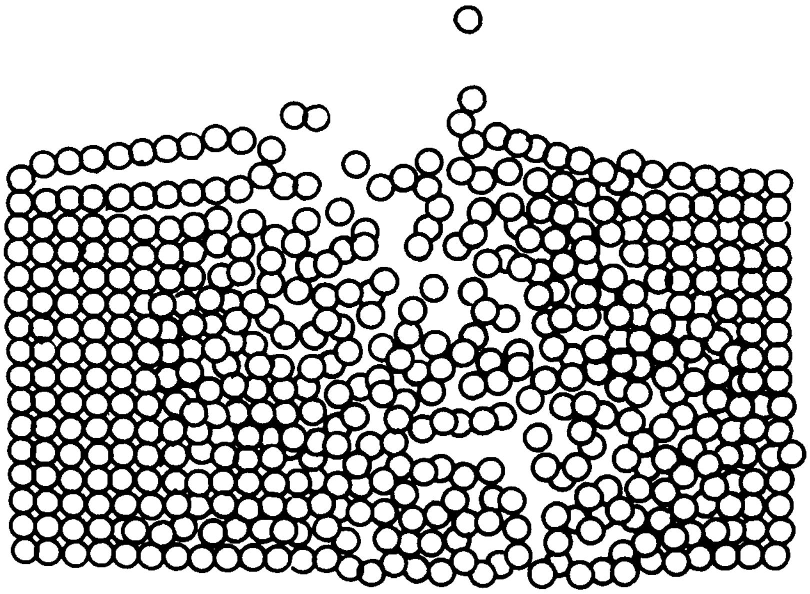


FIGURE 1

IMPACT OF FAST HEAVY PARTICLE ON SOLID SURFACE

Reproduced from Barber et. al.(1): molecular dynamics simulation of sputtering of solid KCl by 1.33 keV Ar+ ions incident at 20° to the surface.

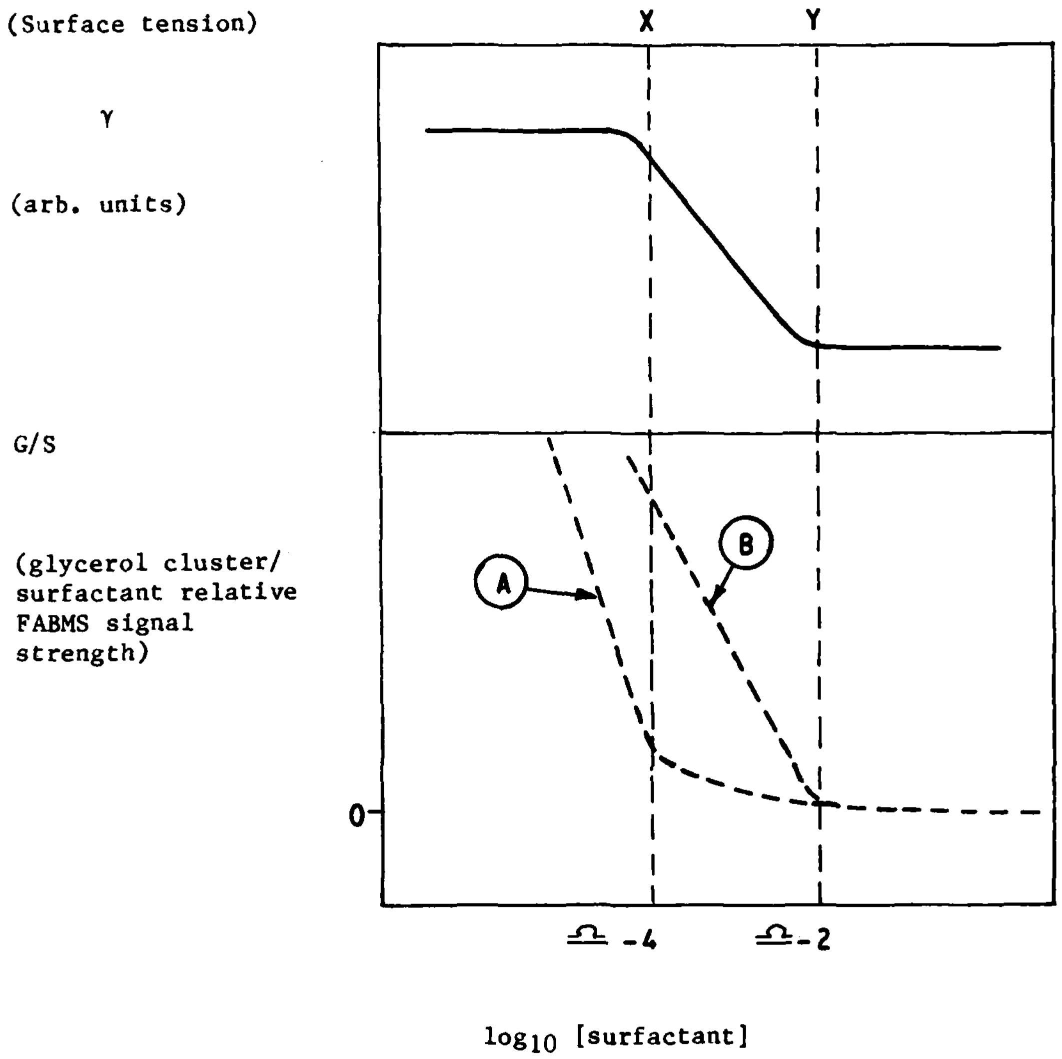


FIGURE 2

DEPENDENCE OF FABMS SURFACTANT SPECTRA ON CONCENTRATION IN GLYCEROL

[Form of results taken from the work of Barber et. al.(6)]

At concentrations below X, the submonolayer region, there is no coherent surface layer of surfactant molecules. The monolayer develops from an expanded form at X to completion at Y, which is termed the "critical micellar concentration" (cmc).

Surfactants can be anionic (R^-X^+, X = group I or II element), cationic (R^+Y^-, Y = halogen) or nonionic (M).

The curve A represents signals due to preionised species (R^+,R^-) and curve B represents ions formed by intermolecular reaction ($RX_2{}^+$, $RY_2{}^-$, $[M + H]^+$, $[M - H]^-$). In both cases, no signals from glycerol clusters are seen above the cmc, and hence G/S = 0.

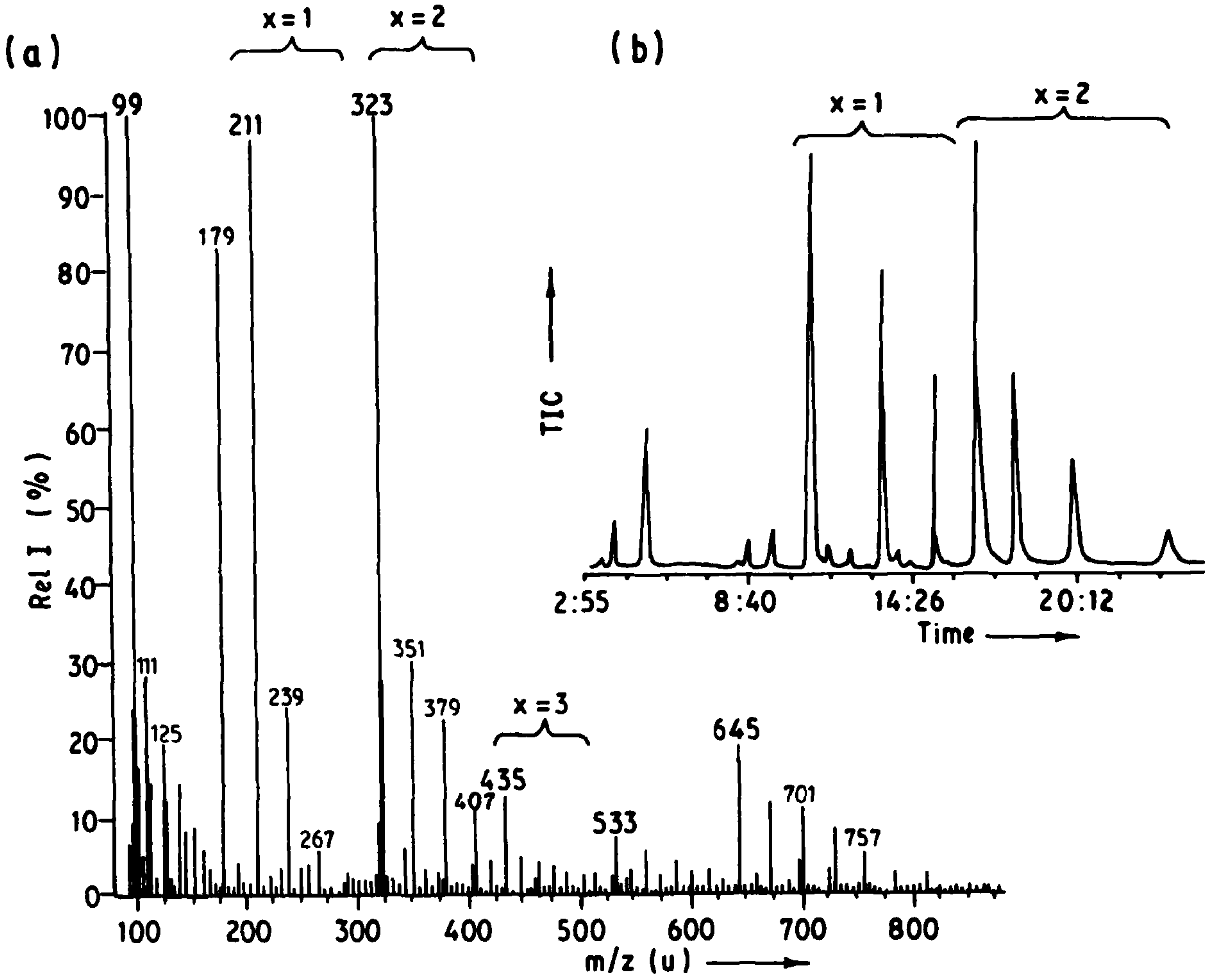
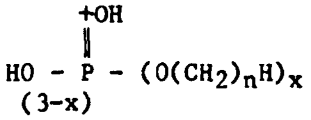


FIGURE 3

SPECTRA FROM GEAR OIL ADDITIVE

(a) +ve ion spectrum showing pseudomolecular ions of the form:



$$\mathrm{HO}_{(3-x)} - \overset{+\mathrm{OH}}{\overset{\|}{\mathrm{P}}} - (\mathrm{O(CH_2)_nH})_x$$

where $n = 8, 10, 12 \ldots$
$x = 1, 2$ mainly

x	MH+			
0	99			
1	211	239	267	
2	323	351	379	407
3	435	463	441	519

(b) (insert) capillary GC/MS chromatogram of methylated derivative (from reference 12).

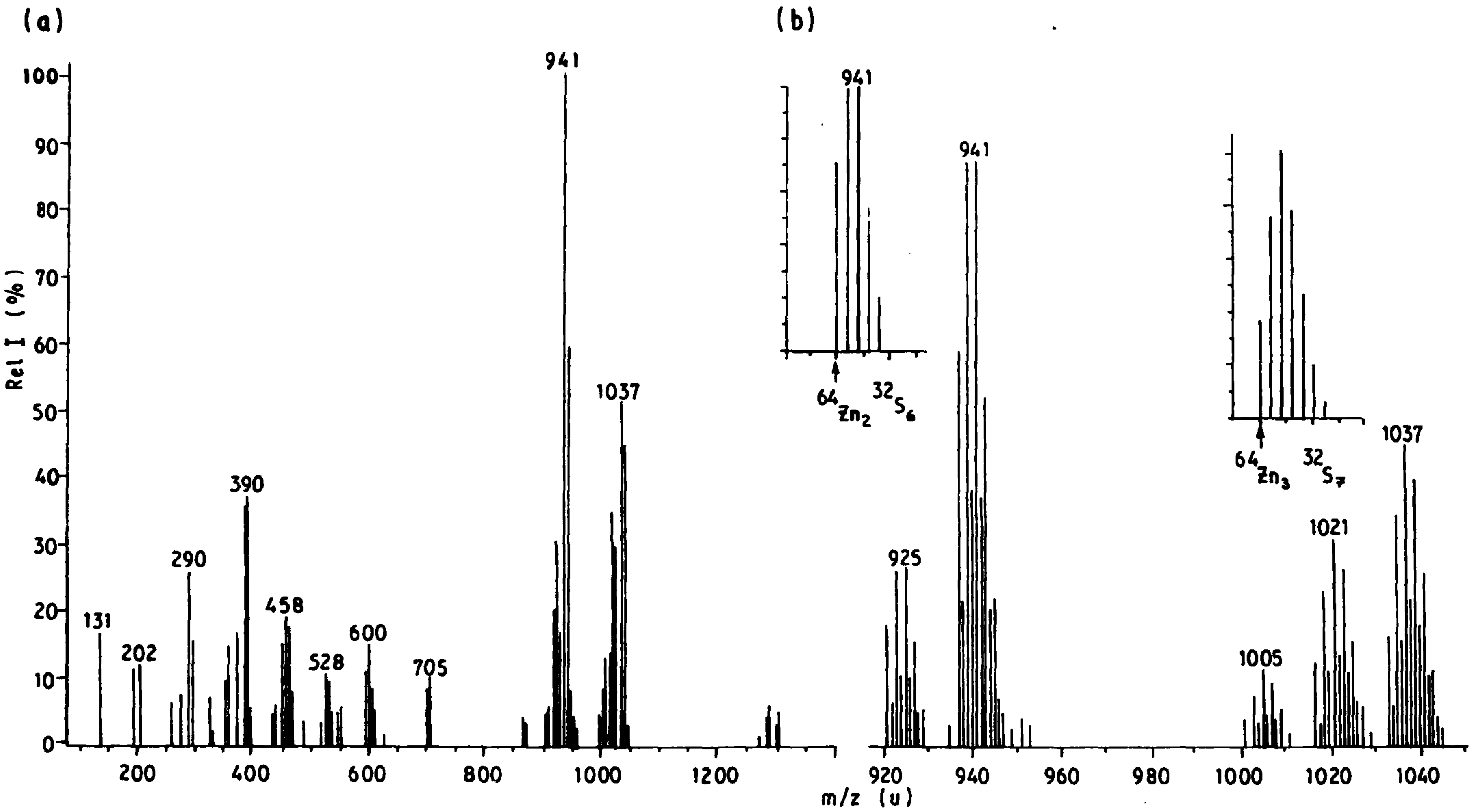


FIGURE 4

SPECTRUM FROM ZINC DIPENTYLDITHIOPHOSPHATE

(a) shows the complete +ve ion spectrum obtained directly from the ZDDP.
(b) shows the higher mass region on an expanded mass scale.
Calculated isotopic distributions are shown.

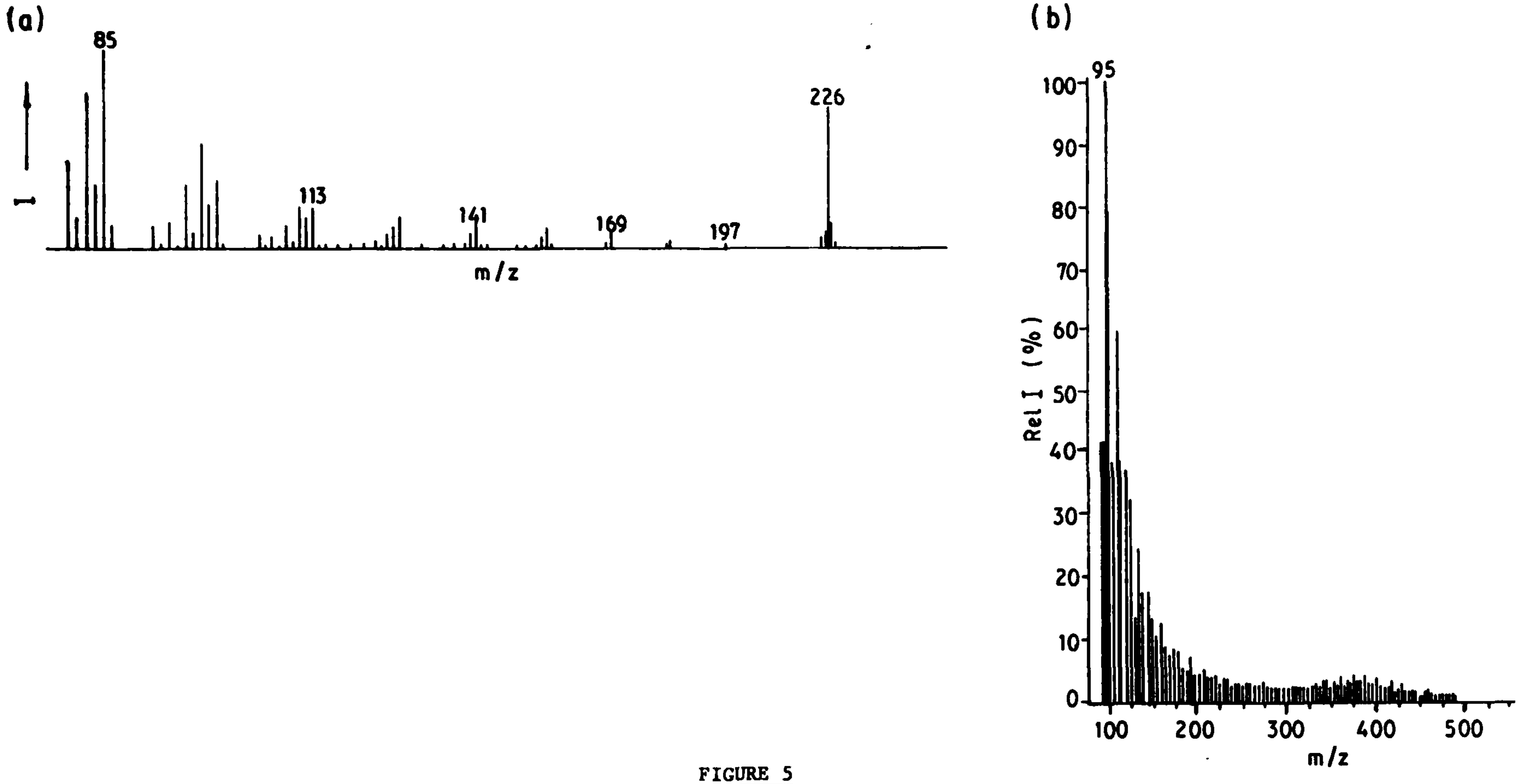


FIGURE 5

SPECTRA FROM HYDROCARBONS

(a) +ve ion spectrum from n-hexadecane (MW 226 u).
(b) +ve ion spectrum from ER5A reference hydrocarbon base oil.

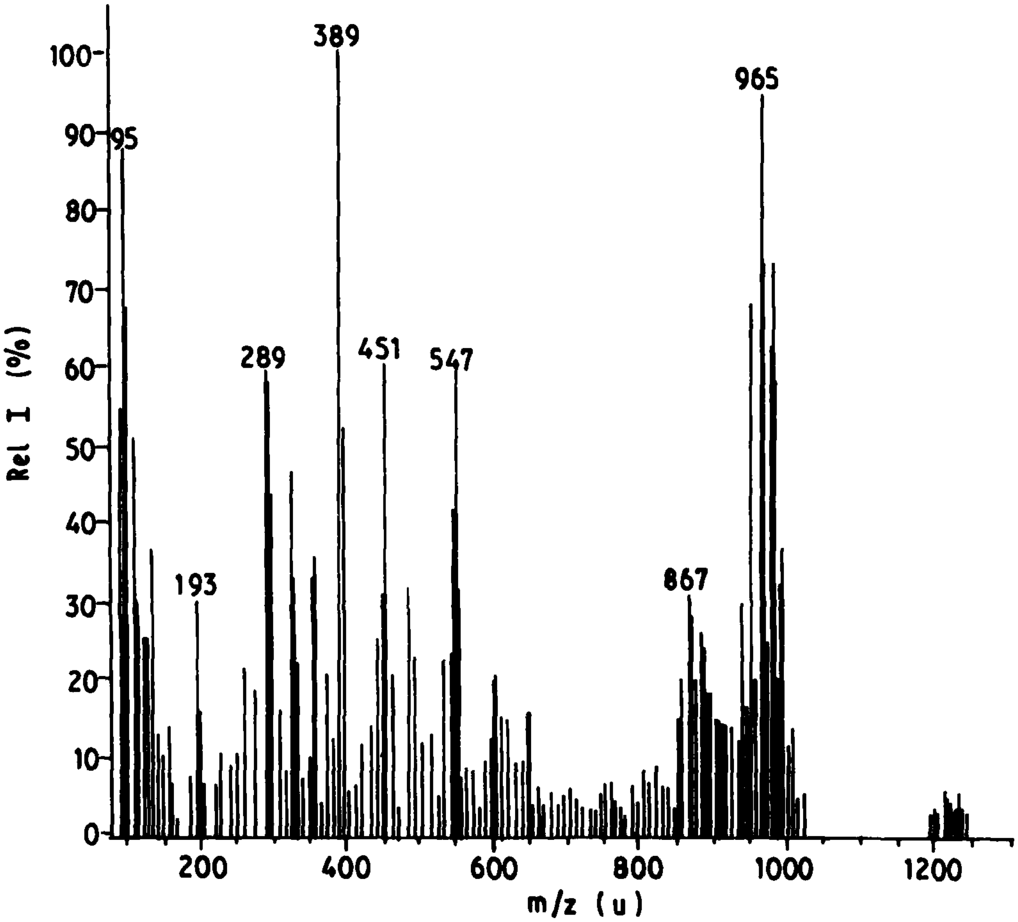


FIGURE 6

POSITIVE ION SPECTRUM FROM A PROPRIETARY ZDDP ADDITIVE PACKAGE

BASED ON A MIXTURE OF C_4- AND C_5- ALCOHOLS

Note the similar form of the spectrum in Figure 4(a). The most intense high mass cluster ions are at m/z 865 ($^{64}Zn_2$) and 961 ($^{64}Zn_3$).

These are consistent with a mean alkyl chain length of between 4 and 5 C atoms (see Table 2).

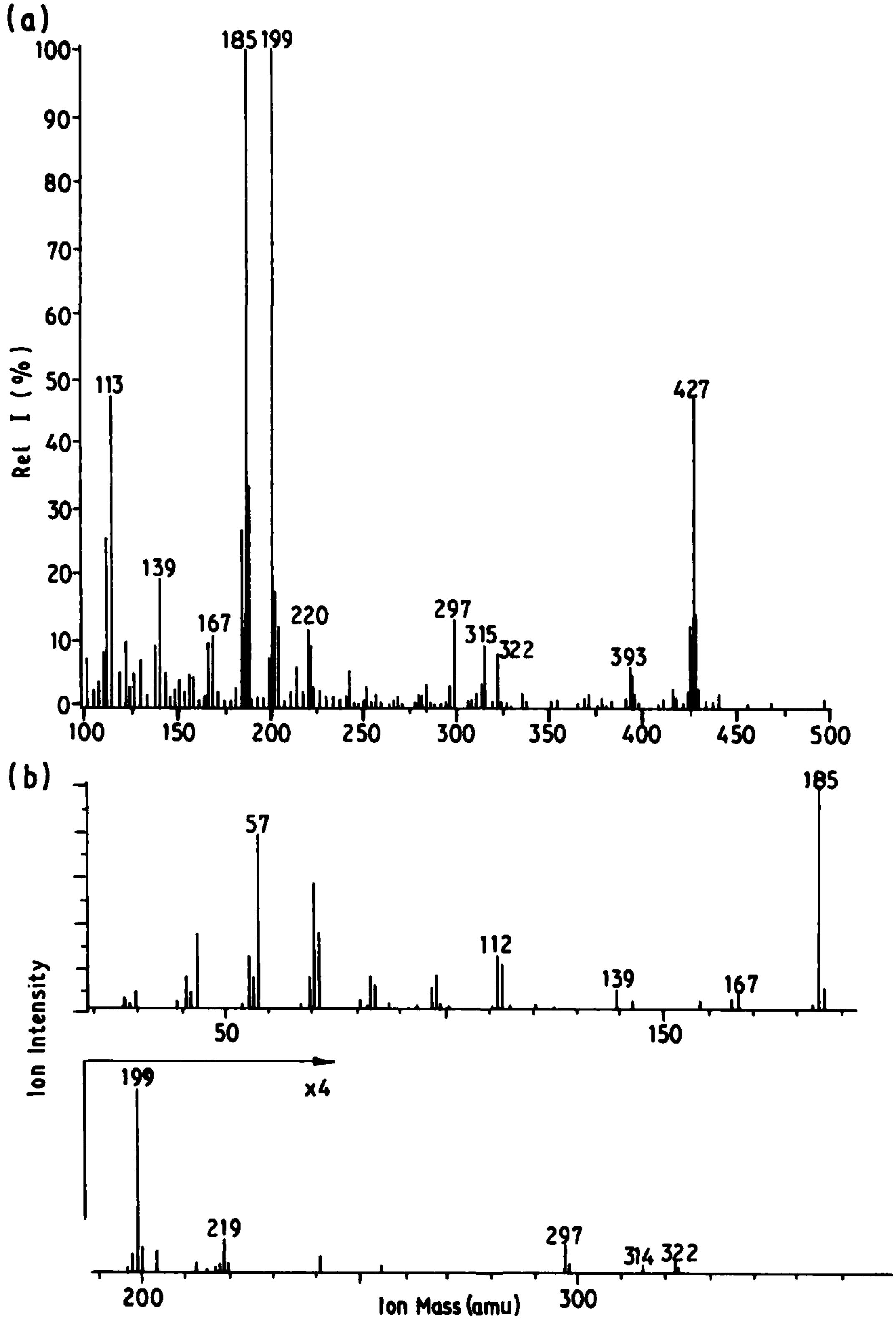


FIGURE 7

EI AND FAB SPECTRA OF A SYNTHETIC ESTER LUBRICANT

(a) FAB and (b) EI spectra contain ions due to the base oil - dioctyl sebacate (MW 314; m/z 112, 113, 185, 297) - and the following additives:

4% phenothiazine (MW 119 u; m/z 167)

1% phenyl-α-naphthylamine (MW 219 u)

1% dioctyldiphenylamine (MW 393 u; m/z 322).

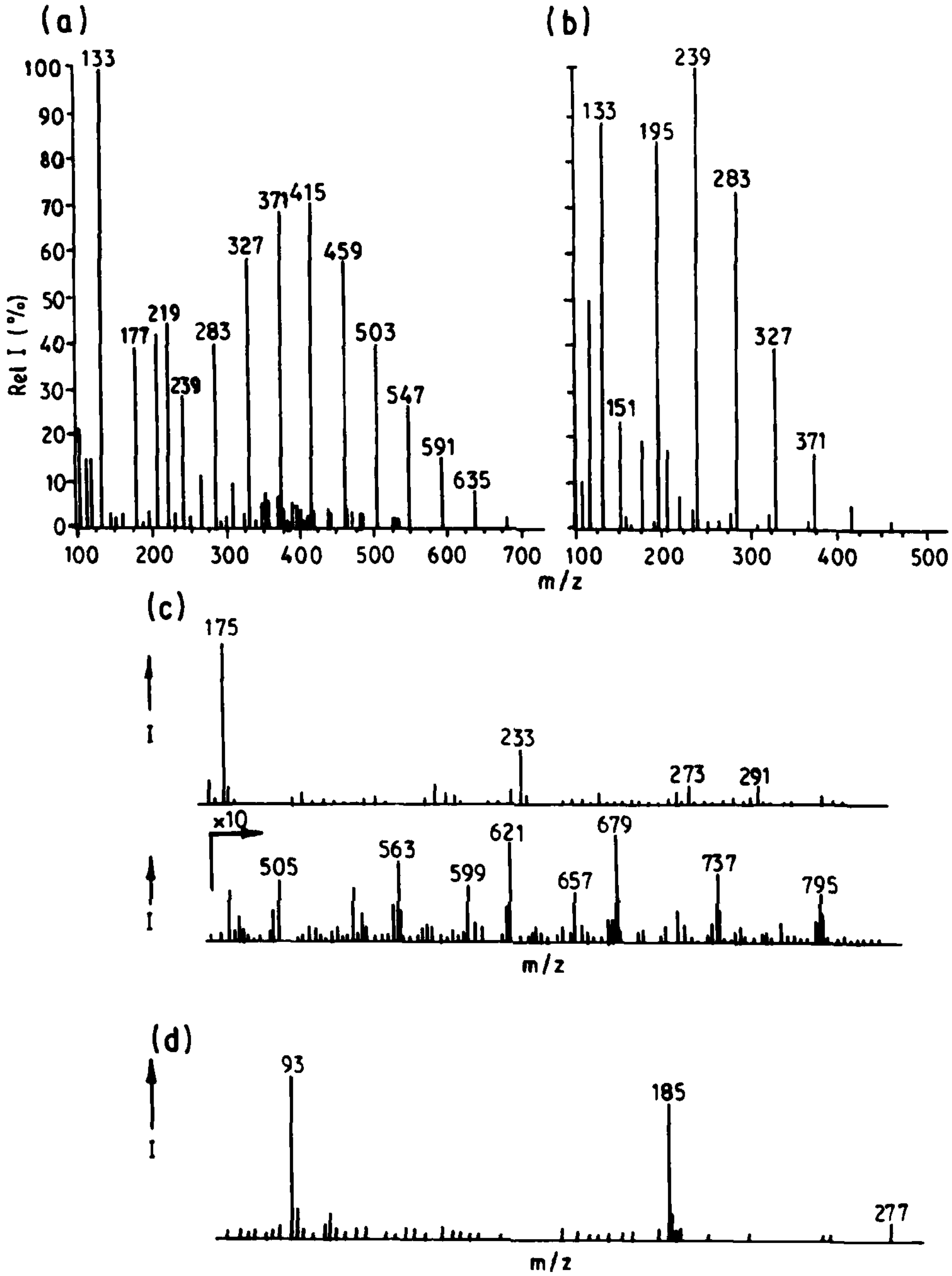


FIGURE 8

POSITIVE ION SPECTRA FROM LIQUID POLYGLYCOLS

Spectra (a) and (b) are from polyethylene glycols of mean MW 400u and 200u respectively. Strong pseudomolecular ions of the type

$\overset{+}{H_2O} - (CH_2CH_2O)_n - H$ with n ~ 6-11 (a); n ~ 4-6 (b)

are seen, together with fragment ions (m/z 133, 177...).

Spectrum (c) is from polypropylene glycol of mean MW 750u, with NaOH added to enhance formation of pseudomolecular ions. [M + Na]+ (m/z 505, 563, 621 ...) and [M + H]+ (m/z 541, 599 ...) ion series are seen, but are weak in comparison with fragment ion series (m/z 175, 233, 291 ...).

Spectrum (d) is from glycerol, showing cluster ions (m/z 93 + 92 n).

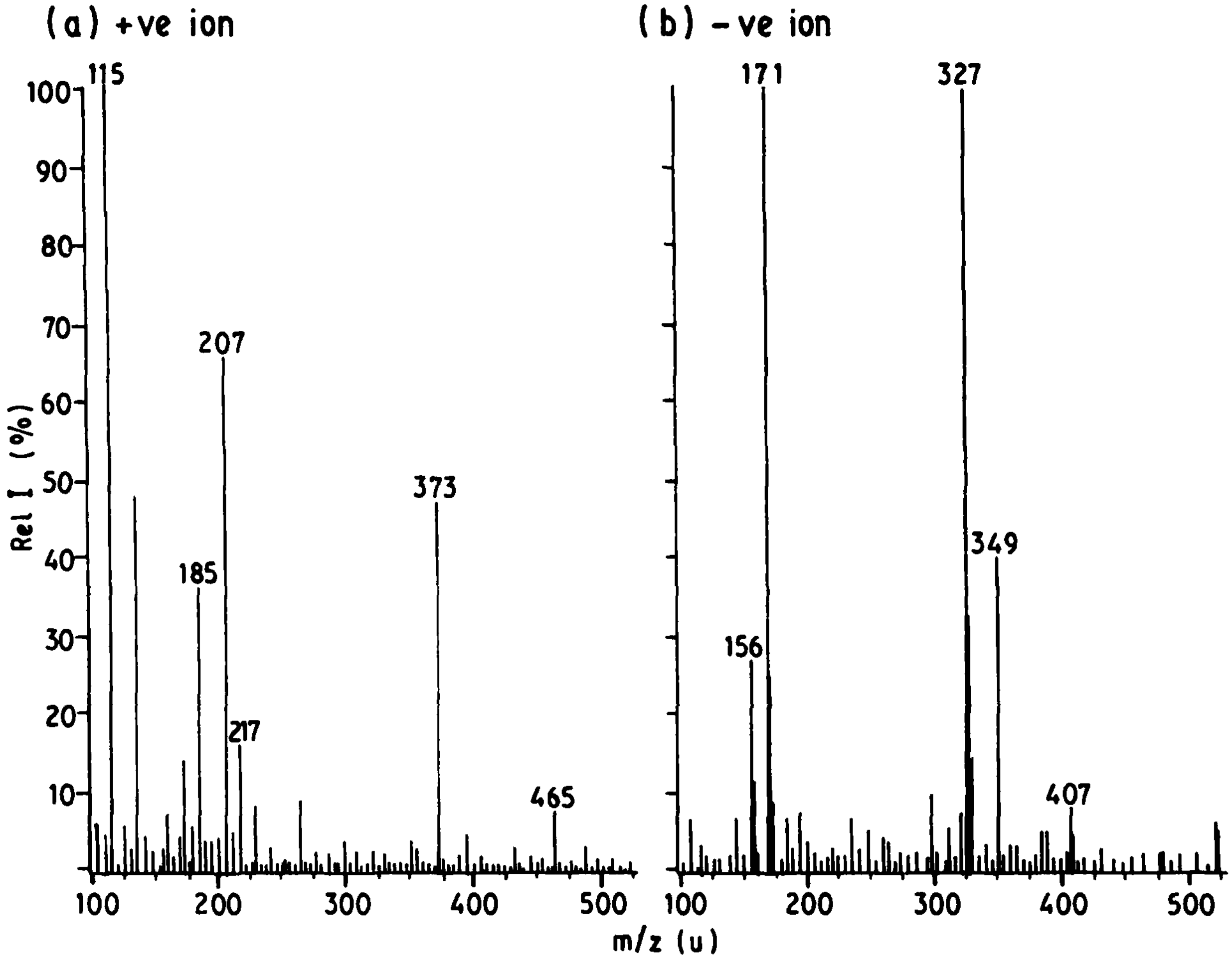
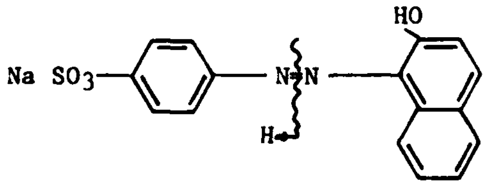


FIGURE 9

+ve AND -ve ION SPECTRA OF A SULPHONATED AZO DYE

Acid Orange 7:
(MW 350 u)



Pseudomolecular ions are intense in +ve ion ([M + Na]+, m/z 373) and -ve ion ([M - Na]-, m/z 327; [M - H]-, m/z 349) spectra. The curly arrow indicates the site of azo-cleavage fragmentation giving ions at m/z 171 (-ve ion) and m/z 217 (+ve ion). Note that glycerol adduct ions (m/z 115, 207 $[Gly_n + Na]^+$; m/z 465 [M + Gly + Na]+) are strong in the +ve ion spectrum.

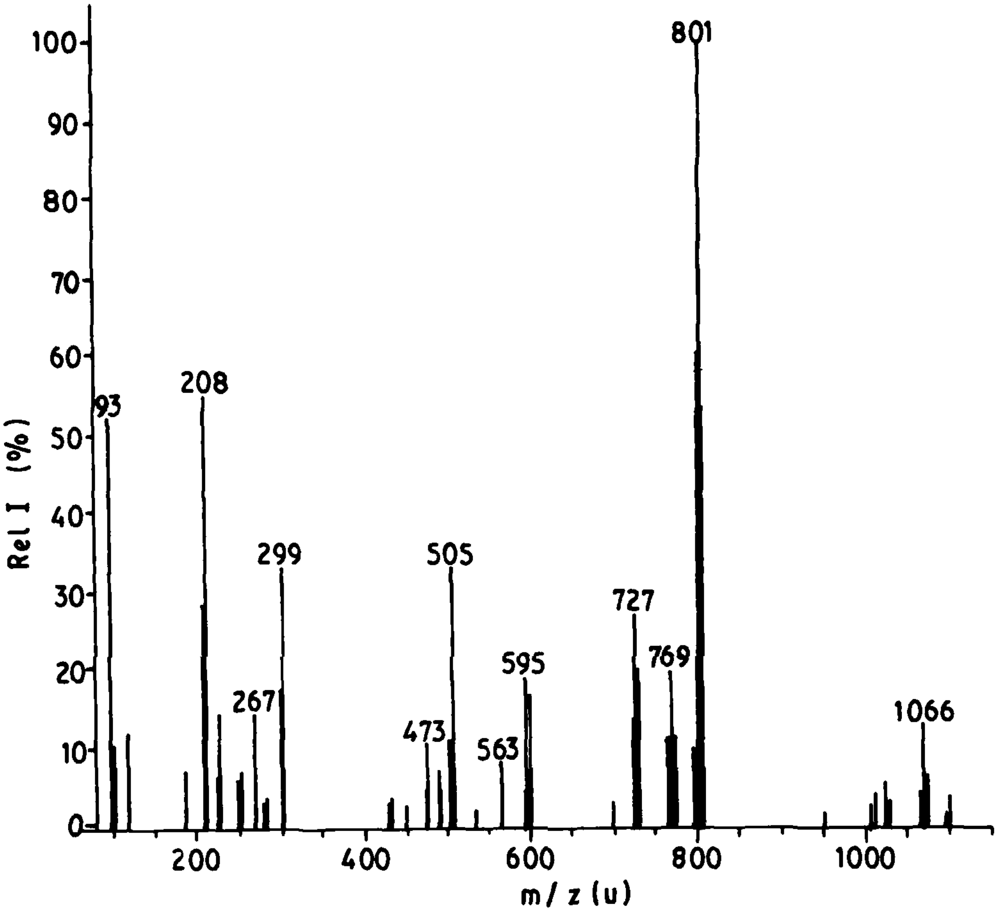


FIGURE 10

POSITIVE ION SPECTRUM FROM LEAD ACETATE TRIHYDRATE IN GLYCEROL

As shown below, most of the cluster ions can be assigned to adducts of Pb and glycerol. Signs of the anion are weak.

Lowest m/z of cluster ion	Assignment	Lowest m/z of cluster ion	Assignment
206	$^{206}Pb^+$	561	$^{206}Pb_2^{4+}$ Gly^{2-}, AcO^-
265	$^{206}Pb^{2+}$ AcO^-	593	$^{206}Pb_2^{4+}$ $(2Gly)^{3-}$
297	$^{206}Pb^{2+}$ Gly^-	725	$^{206}Pb_3^{4+}$ Gly^{2-} OH^-
471	$^{206}Pb_2^{2+}$ AcO^-	767	$^{206}Pb_2^{4+}$ Gly^{2-} AcO^-
503	$^{206}Pb_2^{2+}$ Gly^-	799	$^{206}Pb_3^{4+}$ $(2\ Gly)^{3-}$

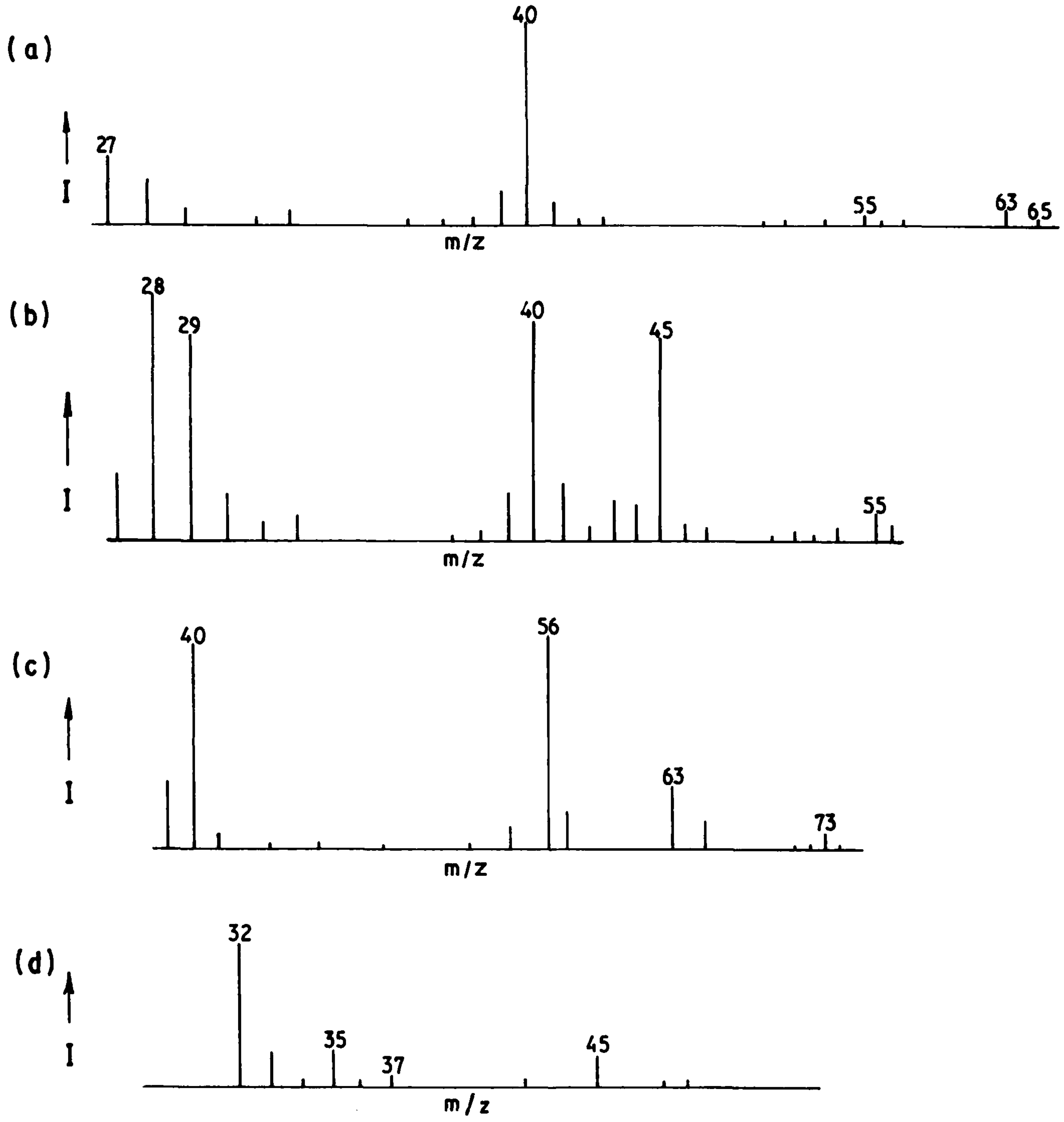


FIGURE 11

SPECTRA FROM INORGANIC SOLIDS

Powder samples were mounted on the Cu target using double-sided adhesive tape.

(a) Background from adhesive tape (+ve ion): Ar(m/z 40), Cu (m/z 63, 65), tape (m/z 27, 55).

(b) +ve ion spectrum from silica gel: Si^+ (m/z 28), SiH^+ (m/z 29), Si^+OH (m/z 45).

(c) +ve ion spectrum from iron oxide (rust): Fe^+ (m/z 56), Fe^+OH (m/z 73).

(d) −ve ion spectrum from zinc sulphide: S^- (m/z 32), Cl^- (m/z 35, 37).

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7. Title

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7a. Title in Foreign Language (in the case of translations)

7b. Presented at (for conference papers). Title, place and date of conference

8. Author 1, Surname, initials	9a Author 2	9b Authors 3, 4...	10. Date	pp	ref
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15. Descriptors (or keywords)

FAST ATOM BOMBARDMENT	ADDITIVE
MASS SPECTROMETRY	REVIEW
FABMS	APPLICATION
LUBRICANT	IONISATION TECHNIQUE

continue on separate piece of paper if necessary

Abstract The fast bombardment (FAB) ionisation source for mass spectrometry (MS) is introduced, and the advantages over other ionisation techniques are discussed. Experimental factors are fully described. In initial work, FABMS is applied to the direct analysis of lubricant additives, thermally labile or involatile organic compounds such as macromolecules and ionic dyestuffs, and inorganic compounds. Applications published in the literature are reviewed. Attention is drawn to the high specificity of FABMS for surfactant species since these are often difficult to analyse by other methods.

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