

Consecutive Reactions in Triple Analyzer Mass Spectrometry and Applications to Mixture Analysis

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A unique application of triple analyzer mass spectrometers is based on the capability for observing consecutive collision-induced reactions in various zones of the instrument. Ions are activated in the first field free region and a specific decomposition product is selected by using the first two analyzers—an electrostatic and a magnetic sector. The ion is then submitted to collisional activation in the third field free region, and the decomposition products are analyzed by using the third sector, a second electrostatic analyzer. It is demonstrated that high-quality spectra can be obtained which compare favorably with normal mass spectrometry/mass spectrometry spectra. Two applications shown to be feasible involve analysis of mixtures of ions which are isobaric and isomeric, respectively.

Triple analyzer mass spectrometers consisting of electric and magnetic sectors have several unique capabilities. If designed properly, they can be used to study the unimolecular (metastable) or collision-induced decomposition of a highly resolved ion beam (1). Additionally, methods can be developed in which sequential chemical reactions (either unimolecular or collision induced) of ions can be observed in the field free regions between the analyzers. In this paper, we demonstrate this latter capability and identify problems in the analysis of mixtures which can be approached with this methodology.

The underlying principles of the method can be understood by considering the difference between conventional mass spectrometry and mass spectrometry/mass spectrometry (MS/MS). In the former, both ionization of the sample and the subsequent chemical reactions which yield structural information occur in the source. In MS/MS, on the other hand, the processes of ionization and reaction occur in physically separate regions. This allows an ion of interest to be separated from interferences and its unique reactions observed. In cases where chemical noise is high in the normal spectrum because of matrix effects, the reactions can be studied under conditions of improved signal-to-noise ratios. The advantages for the analysis of mixtures have been demonstrated in previous papers (1-4).

It is appropriate to inquire whether a further stage of reaction might be of value. For such an experiment to yield unambiguous results, it requires that three independent stages of mass analysis be utilized, one to select the ion beam from the source and the other two to select the products from each of the subsequent two reactions. Furthermore, there is the requirement that the reactions occurring in the additional stage be sensitive to ion structure. This criterion is fulfilled by high-energy, collision-induced dissociations (5-7). Therefore, it follows that ions, produced in the first stage of reaction in either collision-induced or unimolecular (metastable) processes, can be characterized by using a second stage of reaction followed by mass analysis. Investigations into the

ion chemistry upon which MS/MS relies may be facilitated by recourse to such experiments done with two stages of reaction and three of mass analysis.

Observation of consecutive metastable dissociations is not new (8, 9). In fact, triple analyzer mass spectrometers have been applied to these processes, and they have found some use in investigations of ion chemistry. The product ion of a unimolecular dissociation can be examined by mass-selection and collision-induced dissociation and this provides a valuable new source of data on metastable ion reactions (10, 11). While two analyzer mass spectrometers can be used to monitor consecutive reactions (12, 13), the approach is subject to artifacts. The use of a three-analyzer spectrometer is expected to bring about improvements analogous to those found when two-analyzer mass spectrometers took the place of simple magnetic sector instruments for studies of metastable ion decompositions.

In the following, we discuss the extension of a triple analyzer mass spectrometer to consecutive collisional processes. We show (i) that spectra of high quality can be obtained within short data acquisition periods and (ii) that these data have value in certain types of problems in mixture analysis.

EXPERIMENTAL SECTION

The instrument on which these consecutive collision-induced dissociations were performed was the Kratos MS50-TA. The instrument, discussed elsewhere (1), is a high-resolution mass spectrometer of conventional geometry with a third sector, an electrostatic analyzer, following the magnetic sector. The reaction sequence utilized for these experiments is illustrated in Figure 1, which also indicates the sequence of sectors and the three separate reaction regions of the instrument. In this study, ions emerging from the source are activated in the first reaction region. A specific fragment ion is then transmitted to the third reaction region by setting both the first electric sector and the magnetic sector to the appropriate values. The ion m_2^+ is then itself collisionally dissociated. Mass analysis of the resulting fragment ions is accomplished by scanning the final electric sector. Conventional MS/MS spectra on selected ions are taken by mass analysis using the first two sectors in tandem and allowing dissociation to occur in the third field free region followed by mass analysis with the electric sector.

An electron ionizing energy of 70 eV and a total emission current of 500 μ A were used for these experiments. The ion accelerating voltage was 8000 V. The gas pressure in the second collision cell was measured in the adjacent vacuum housing as 1.5×10^{-6} torr and resulted in a 20% suppression of the main beam intensity compared to the value in the absence of the gas. The gas pressure in the first collision cell was adjusted to maximize the beam intensity for the consecutive reaction (nominal pressure 1×10^{-5} torr). Helium was employed as collision gas in both cells and in all experiments. Samples were introduced into the source (temperature 140 °C) from a reservoir via a molecular leak. None of the reported spectra are corrected for contributions from unimolecular dissociations which were no more than a few percent of the corresponding CID signals.

All materials were obtained from commercial sources and gave mass spectra in accord with literature reports.

CONSECUTIVE CID REACTIONS

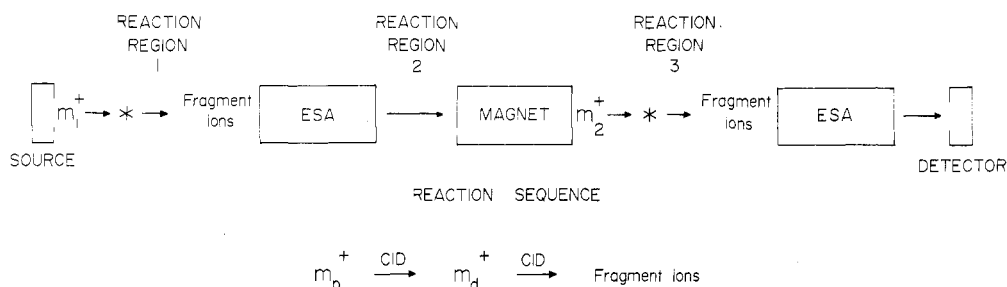


Figure 1. Schematic representation of the reaction sequence used for the described experiments.

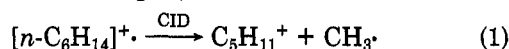
Table I

precursor	ion of interest	reaction region	
		1	3
<i>n</i> -hexane	86 ⁺	CID → 71 ⁺	CID → fragments
<i>n</i> -decane	113 ⁺	CID → 71 ⁺	CID → fragments
2-pentanone	86 ⁺	CID → 71 ⁺	CID → fragments
3-methyl-2-butanone	86 ⁺	CID → 71 ⁺	CID → fragments

RESULTS AND DISCUSSION

$C_5H_{11}^+$. The alkanes have been used in earlier tests of the capabilities of MS/MS, including characterization of the original mass-analyzed ion kinetic energy spectrometer (14) and the earliest linked scan method (15). The MS/MS spectra contain a number of alkyl cations, and these, in turn, give rich CID spectra. Therefore, $C_5H_{11}^+$ (m/z 71) was chosen for the initial test of the multiple reaction capability (see Table I).

As a reference point, the CID spectrum of $C_5H_{11}^+$ was recorded in the usual MS/MS mode. Following that, $C_5H_{11}^+$ was formed by CID from the molecular ion of *n*-hexane (eq 1) in the first field free region, transmitted to the collision cell



in the third field free region and activated by collision to yield a CID spectrum. The intensity of $C_5H_{11}^+$ produced in the CID of the molecular ion of hexane was approximately 6% of the most intense reaction product, $C_4H_9^+$.

The $C_5H_{11}^+$ ion was then produced in the first reaction zone from *n*-decane. Examination of the CID spectrum of *n*-decane revealed that 71⁺ now adjoined a more intense m/z 70 and was a relatively small percent of the total collision-induced products. Again, $C_5H_{11}^+$ produced in the first reaction zone was transmitted to the second zone and collisionally activated.

The three spectra of $C_5H_{11}^+$ were identical in terms of products formed. However, the intensity of m/z 43 was smaller relative to other product ions in the spectra resulting from the two-stage experiment. Furthermore, these spectra exhibited lower signal to noise and slightly lower resolution presumably because of the greater angular divergence and kinetic energy spread of the m/z 71 beam produced in the first reaction zone compared to the source-produced beam.

$C_4H_7O^+$. This ion also has a nominal mass to charge ratio of 71 and is produced in the mass spectra of 2-pentanone and 3-methyl-2-butanone. If the ions maintain the structures corresponding to their neutral precursors, they will exist as isomers $CH_3CH_2CH_2CO^+$ (1) and $(CH_3)_2CHCO^+$ (2). These ions are also the most intense in the CID spectra of the molecular ions of 2-pentanone and 3-methyl-2-butanone.

Again, the normal CID spectra of m/z 71 ($C_4H_7O^+$) were obtained as benchmarks (Figure 2). There are few differences in the spectra of these source-produced isomeric acylium ions.

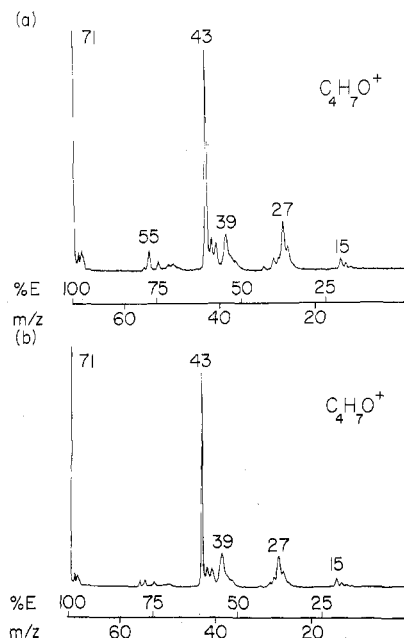


Figure 2. CID spectra of (a) the 71⁺ ion formed in the source from 2-pentanone and (b) the 71⁺ ion formed in the source from 3-methyl-2-butanone.

For example, we see that m/z 55 and the multiplet, m/z 26–29, are relatively more intense for the *n*-propyl case (structure 1).

In Figure 3, we give the CID spectra of m/z 71 ions produced by collisional activation in the first reaction zone. It is now evident that the slight differences seen in the normal CID spectra of these isomeric ions are amplified in the multireaction method. The intensities of ions in the m/z 50–55 and in the m/z 26–31 regions are considerably greater for structure 1. This observation can be interpreted in terms of less extensive isomerization or interconversion of the higher energy, collisionally produced $C_4H_7O^+$ ions. Stated differently, stepwise transformation of the molecular ion appears to be associated with better retention of structural identity. More investigation of this phenomenon is required to establish its generality.

Mixture Analysis: Isobars. Given the high quality of the MS/MS spectra obtained in the double collision sequence, attention can be turned to model systems which illustrate potential capabilities in chemical analysis. A mixture of 3-heptanone and *n*-pentane was chosen as an illustration. The molecular ion of 3-heptanone gives as a major ion in its mass spectrum m/z 72, $[C_4H_8O]^+$, which is formed by alkene loss via the McLafferty rearrangement. If the structure of this particular ion is to be investigated by means of collision-induced dissociation in the presence of an isobaric contaminant (for example, *n*-pentane molecular ion, also m/z 72), it would lead to a daughter ion spectrum for the ion of nominal mass

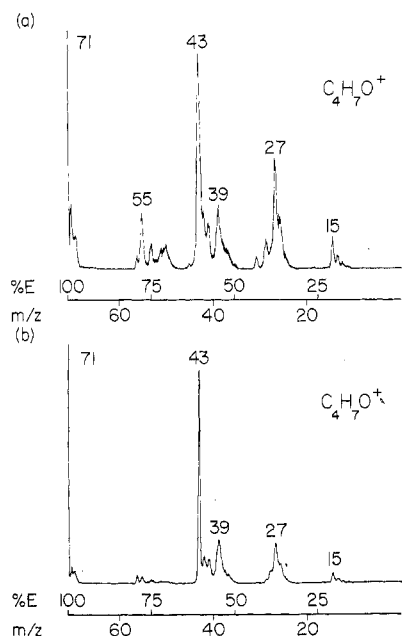


Figure 3. CID spectra of (a) the 71^+ ion produced from the molecular ion of 2-pentanone by a prior collision and (b) the 71^+ ion produced from the molecular ion of 3-methyl-2-butanone from a prior collision.

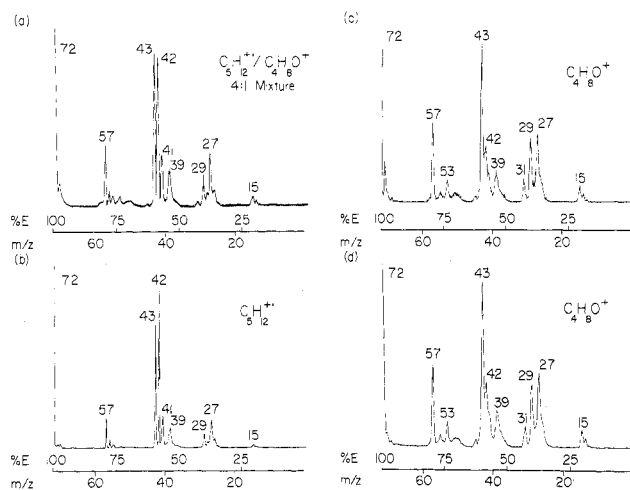


Figure 4. CID spectra of (a) the ion of nominal mass 72 formed in the source from a 4:1 pentane/3-heptanone mixture (not mass resolved), (b) the molecular ion of *n*-pentane, m/z 72, (c) the 72^+ ion produced from 3-heptanone in the source, and (d) the 72^+ ion of 3-heptanone formed from the molecular ion in a prior collision (in the presence of the contaminant *n*-pentane).

72, which is the sum of the spectra of the individual precursor ions (Figure 4a). In mixture analysis, one goal would be to identify the structure of a molecular ion (here *n*-pentane) occurring at the same mass as the fragment ion of a higher mass contaminant (3-heptanone). These situations would require spectral subtraction and be subject to error if the experiment were performed by use of a nonselective ionization technique on a two sector instrument. Obtaining the spectrum of one of the components would permit more reliable spectral subtraction.

The capabilities of the triple analyzer instrument, on the other hand, are such as to offer two solutions to the problem. One is to utilize the high-resolution capability of the first two sectors to uniquely select only one of the isobaric precursor ions for transmission into the third reaction region for further analysis (i.e., high-resolution mass spectrometry/mass spectrometry as discussed elsewhere (1, 16, 17)). The second alternative is to apply the specificity provided by the first two analyzers to selectively transmit that 72^+ ion which is a

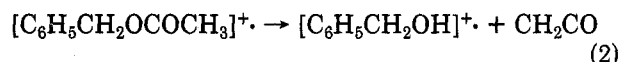
Table II

precursor	ion of interest	reaction region	
		1	3
pentane	72^+		CID → fragments
3-heptanone	72^+		CID → fragments
3-heptanone	114^+	CID → 72^+	CID → fragments
mixture	nominal 72^+		CID → fragments
mixture	114^+	CID → 72^+	CID → fragments

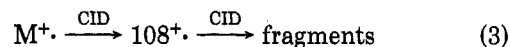
fragment of the collision-induced dissociation of a particular precursor ion into the third reaction region. Figure 4 shows the spectra obtained for 72^+ ions generated both in the source and in the first reaction region by the processes illustrated in Table II.

Comparison of the normal MS/MS spectra of the isobaric m/z 72 ions shows significant differences, as expected (see Figure 4b,c). Now, the consecutive reaction method is applied to the problem, and we see that the CID spectra of m/z 72, produced by activation of the molecular ion of 2-heptanone in zone 1, is that of $[C_4H_8O]^+$, despite the presence of the *n*-pentane in the source of the mass spectrometer (see Figure 4d). Indeed, the relative abundances of all peaks in the double collision sequence agree within $\pm 3\%$ relative abundance with those in the normal MS/MS spectrum of $[C_4H_8O]^+$ generated in the ion source containing pure 2-heptanone.

Mixture Analysis: Isomeric Ions. A more difficult problem is illustrated by the analysis of benzyl acetate in the presence of *o*-cresol. Elimination of ketene from the molecular ion of benzyl acetate yields an ion 108^+ in the mass spectrum of benzyl acetate (eq 2) which is an isomer of ionized *o*-cresol,



and analysis by MS/MS (using 108^+) is precluded by the multiple origins of this ion. Unlike the previous example, in which high-resolution MS/MS provided a solution to the difficulty, in this case there exists only the alternative of two-step collision-induced dissociation. The molecular ion is dissociated consecutively according to the reaction sequence



Approximately a 30:1 mixture of *o*-cresol and benzyl acetate was admitted to the source of the triple analyzer and a normal MS/MS spectrum taken of m/z 108 (Figure 5a). Comparison with authentic MS/MS spectra of *o*-cresol and the $[C_7H_8O]^+$ formed in the decomposition of the benzyl acetate molecular ion (Figure 5b,c, respectively) reveals that the mixed spectrum is dominated by the presence of the *o*-cresol molecular ion. This is not surprising in view of the predominance of this component in the mixture. The spectrum of $[C_7H_8O]^+$ from benzyl acetate, the minor component, was then obtained by using the consecutive collision-induced reaction capability represented by eq 3 (see Figure 5d). The spectrum is very similar to the normal MS/MS spectrum of $[C_7H_8O]^+$ from benzyl acetate; note the lower relative intensities of m/z 92, 91, and 90 and m/z 77 with respect to m/z 79, for example (vide supra). We cannot rule out a small contribution from the molecular ion of *o*-cresol, however.

In view of these initial results it seems evident that consecutive collision-induced dissociation reactions can serve both as an alternative to high-resolution precursor ion analysis in cases of isobaric mixtures and as the *only* experimental approach for mixtures of isomeric ions associated with different

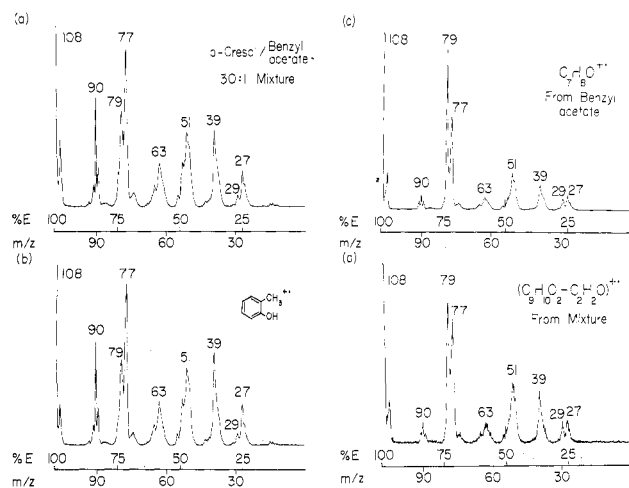


Figure 5. CID spectra of (a) the 108⁺ ion formed in the source from a 30:1 *o*-cresol/benzyl acetate mixture, (b) the molecular ion of *o*-cresol, *m/z* 108, (c) the 108⁺ ion formed in the source from benzyl acetate, and (d) the 108⁺ ion produced by prior collision of the molecular ion of benzyl acetate.

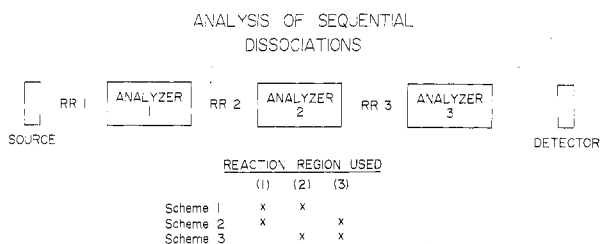


Figure 6. Schematic representation of a triple analyzer instrument illustrating the three possible modes of consecutive reaction monitoring.

precursor ions. There are of course several other areas which can be envisioned as benefiting from further pursuit of this technique. Specifically, this includes ion structure analysis in those particular cases where the time scale may affect the nature of the product (18–20). A second area open to the application of this methodology is the structural identification of large organic molecules. An example of the type of problem is an information-poor collision-induced dissociation spectrum produced, for example, from a sample component which gives one dominant loss process (loss of H₂O is typical). Additional structural information can be obtained by submitting the dominant collision fragment (e.g., M – H₂O) to a second stage of reaction. Work in one of our laboratories which exemplifies such a problem is the collision-induced dissociation analysis of the antileukemia agent 4-β-hydroxywithanolide.

General Instrument Considerations. There are three possible modes of operation for the analysis of two consecutive fragmentation reactions in triple analyzer mass spectrometers of various types (see Figure 6). The schemes given apply to quadrupole as well as sector instruments, where E represents an electric sector, B, a magnetic sector, and Q, a quadrupole analyzer. For a three-analyzer instrument of the EBE geometry (which is the configuration of the instrument used in the present work) the method of choice is that shown as scheme 2. In this configuration both the fragment ion that undergoes the second stage of collision-induced dissociation and the parent ions from which it is derived are uniquely specified by the combination of the first two sectors. This minimizes the possibility of artifacts in the final daughter ion spectrum. The alternative schemes 1 and 3 make different choices of reaction regions and both are more subject to interference. When the first and second reaction regions are chosen (scheme 1), the ions subject to the second stage of reaction have a known kinetic energy (and hence *m*₂/*m*₁ ratio) but they are not uniquely specified. When the final two sectors are linked

and scanned to produce the daughter ion spectrum this ambiguity carries through. Only by an independent measurement of the kinetic energy of the final product ion would the mass-to-charge ratios of each ion in the fragmentation sequence be specified. The third alternative, scheme 3, is subject to even more ambiguity. In this mode, the second and third regions are used and the first electric sector has no function as an analyzer. The experiment reduces to the dual analyzer option.

When one considers alternative types of triple sector mass spectrometers the same sort of analysis is possible. We consider specifically the BEB geometry and show that it does not give equivalent results to the EBE. Scheme 1, using the first and second reaction regions, is equivalent to its counterpart in the EBE geometry. Again, linked scans of the last two sectors are the only convenient means of access to daughter ion spectra but they are subject to ambiguity. Scheme 2 is the counterpart of 2 in the earlier geometry and serves to identify the double collision sequence. The main difference between the EBE and BEB geometry occurs when the second and third regions are selected (scheme 3). In the latter case, the dual reaction sequence is uniquely specified in terms of mass-to-charge ratios of each species.

Finally the triple quadrupole instrument can only be used per scheme 3; otherwise, only one stage of mass analysis is effective. For consecutive reactions the triple quadrupole instrument would need to be equipped with collision cells between the first and second rod assemblies and between the second and third assemblies with all three quadrupoles operating in a mass analysis mode. The difference between the sector and quadrupole geometries arises from the fact that the ion accelerating voltage in conjunction with an energy analyzer serves to provide a mass ratio (*m*₂/*m*₁) measurement, where *m*₂ and *m*₁ refer to the masses of the daughter and parent ions, respectively. This is the reason the first (preanalysis) reaction region is not useful in a strict mass-to-charge analyzer such as the quadrupole.

There are, of course, numerous other possibilities which would result from various combinations of sectors and/or quadrupoles. The only other combinations which shall be considered here are the triple analyzer geometries BEE and EBB. For each of the proposed modes of operation (schemes 1, 2, or 3) the BEE is equivalent to the above described BEB configuration. Likewise, there is complete equivalency between the EBB arrangement and the previously suggested EBE configuration. Although many of these combinations are equivalent from the standpoint of achievable specificity for studying sequential dissociation reactions, each combination may have relative advantages or disadvantages when considering such things as attainable resolution in the selection of precursor or product ions. For example, magnetic sector analyzers will have higher mass resolutions than electric sectors of similar size when used to analyze the products of high-energy collisions (separations based on *mv*/*q* vs. *mv*²/*q*, respectively).

In summary, we note that the MS/MS technique evolved from conventional mass spectrometry in response to the demands of such problems as ion structure determination and complex mixture analysis. The results presented here appear to demonstrate a useful role for increased complexity in mass spectral analysis, viz., from MS to MS/MS to consecutive collision-induced dissociation reactions (MS/MS/MS). Further evaluation will be required in order to assess the generality of this advantage and to optimize the experiment and the instrumentation.

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Effect of Inorganic Contaminants on Field Desorption Mass Spectrometry of Organic Compounds

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The influence of inorganic contaminants on the sensitivity of organic analysis by field desorption mass spectrometry has been studied quantitatively. Several organic compounds were selected as model compounds for different processes of ion formation in field desorption. With the exception of glucose, the observed general tendency was a decrease in sensitivity with increasing amounts of inorganic contaminants. The effect was found to be dependent on the salt anion and on the type of compound. As a consequence, a strategy for the chromatographic workup of biological and environmental samples is outlined which is adapted to the special requirements of field desorption mass spectrometry.

Since the introduction of field desorption (FD) mass spectrometry (MS) (1) this novel ionization technique has had the reputation that it is difficult to obtain reproducible results. On one hand, a large variety of polar and labile model compounds were successfully investigated (2, 3) consistently showing the potential of FD MS as an analytical tool in biochemical analysis; on the other hand, in the analysis of so-called real samples extracted from environmental or biological material, experiences in the use of FD MS ranged from success without problems to complete failures (4). This variable situation most probably can be explained by nonidentical conditions mainly in two areas: firstly, the quality of the FD emitter used and, secondly, the amount and chemical nature of contaminants in the samples under investigation.

A procedure for the reproducible production of high temperature activated FD carbon emitters has been recently described in detail (5). In view of the experience that FD MS is a highly specific technique for organic mixture analysis and

because of the minor effects of organic contaminants on FD sensitivity, this study is concerned with the influence of inorganic contaminants on the sensitivity of organic analysis by FD MS. It can be assumed that most samples of environmental or biological origin contain a substantial and generally nondefined amount of inorganic salts originating either from the crude sample itself and/or from the work-up procedure. The pronounced sensitivity of the FD technique toward inorganic salt impurities found in this study supports the assumption that a large portion of disappointing experiences with FD MS has been caused by inorganic impurities.

In the following, quantitative investigations on the extent and the variability of this salt effect are presented, and a strategy for sample purification adapted to the special requirements of FD MS is given.

EXPERIMENTAL SECTION

Mass spectrometry was performed on a VG ZAB-1F equipped with a FD ion source. All measurements were performed in the double focusing mode. The ion source potentials were +8 kV for the FD emitter and -4 kV for the counterelectrode. High temperature activated carbon emitters (6) were produced on a slightly modified VG activator according to a published procedure (5). The average length of the carbon microneedles was 30 μ m. The signals were accumulated on a multichannel analyzer type Canberra series 80. For the sensitivity tests 250 ng of the compound was completely desorbed under manual heating current control and signal accumulation was performed over the entire desorption process. Comparative sensitivity tests on one compound were performed with a single emitter. The sample solution was applied to the FD emitter by use of a microliter syringe fixed in a three-dimensional micromanipulator and the application procedure was controlled under a stereomicroscope at a magnification of 63 \times . The variations of repeated sensitivity tests using the same FD emitter were found to be about $\pm 20\%$.