minimally detect these emissions on our steady-state spectrophotometer at the most sensitive setting with slits nearly open. Under these conditions first- and second-order scatter peaks can interefere with the detected fluorescence.
(6) Kenney, J. W.; Herold, D. A.; Michl, J.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6884.
(7) O'Boyle, T. E.; Scott, L. J.; Plummer, B. F. *J. Org. Chem.* **1979**, *44*, 514.
(8) Plummer, B. F.; Hopkinson, M. J. "Abstracts of Papers", ACS/CSJ Congress, Honolulu, Hawaii, April 1–6, 1979; American Chemical Society: Washington, D.C., 1979; ORGN 151.
(9) (a) Compound **2**, ref 7. (b) Compound **5** is found in Plummer, B. F.; Chihal, D. M.; D'Orsogna, D. D.; Blenkarn, B. D. *J. Org. Chem.* **1977**, *42*, 4092. (c) Compounds **9** and **10** are found in Hauptmann, S.; Franke, L.; *J. Prakt. Chem.* **1963**, *19*, 180. (d) Compound **11** is found in Trost, B. M.; Brittelli, R. *J. Org. Chem.* **1967**, *32*, 2620. (e) The remaining compounds, excluding **1**, were synthesized by us according to well-known procedures, and all give the correct elemental and spectroscopic analyses. Rigorous purification of all compounds included multiple recrystallizations, column chromatography, and, where possible, vacuum sublimation. Zone refining is eschewed because acenaphthylenes thermally polymerize.
(10) A nitrogen-laser-emitting pulses of 337-nm light of 8 ns fwhm and delivering 2–3 mJ of photon energy was used as the excitation source. A Tektronix R 7912 transient digitizer and a 4010 video graphics terminal were interfaced to a PDP11 T34 computer system and programs written to allow recovery of half-times and to plot in a point-by-point fashion the emission spectrum from each compound: Rodgers, M. A. J.; Foyt, D. C.; Zimek, Z. *Radiat. Res.*, in press.
(11) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience, New York, 1970; p 92.
(12) (a) Kropp, P. J.; Poindexter, G. S.; Pionta, N. J.; Hamilton, C. *J. Am. Chem. Soc.* **1976**, *98*, 8135. (b) Charlton, J. L.; Williams, G. J. *Tetrahedron Lett.* **1977**, 1473.
(13) R. A. Welch Postdoctoral Fellow.

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Selected Fragment Scans of Mass Spectrometers in Direct Mixture Analysis

Sir:

The analytical applications of mass spectrometry derive largely from information on fragmentation reactions of the general type

$$m_1^+ \rightarrow m_2^+ + m_3 \qquad (1)$$

Conventional mass spectra, whatever the ionization method, present abundances integrated over all those reactions which yield each individual product ion. The importance of metastable ions is that particular reactions are examined.[1] When two independent analyzers are employed to study metastable ions (or the analogous collision-induced dissociations), then two quantities in eq 1 can be specified uniquely. Methods are available which allow scans to be made for fixed m_1^+ (detection of all fragments m_2^+ from a selected parent ion)[2] and for fixed m_2^+ (detection of all precursors m_1^+ of a selected fragment ion).[3,4] Selection for either m_1^+ or m_2^+ can be achieved by scanning a single analyzing field given an instrument of appropriate (reversed) geometry.[5]

We now report the first examples[6] of a new method of scanning mass spectrometers such that the neutral fragment mass, m_3, is constant. This procedure allows compounds with particular functional groups to be directly detected in complex mixtures. As such, it should prove complementary to mass-analyzed ion kinetic energy (MIKE) scans which allow individual compounds to be determined.[7] The new procedure maximizes the *chemical* information by selecting only ions which undergo a specified reaction. For example, all anions which undergo the loss of a neutral fragment of 44 mass units can be detected in a single scan (Figure 1); since this reaction is characteristic of carboxylic acids,[9] one has an immediate indication of the presence and molecular weights of any carboxylic acids in a sample.

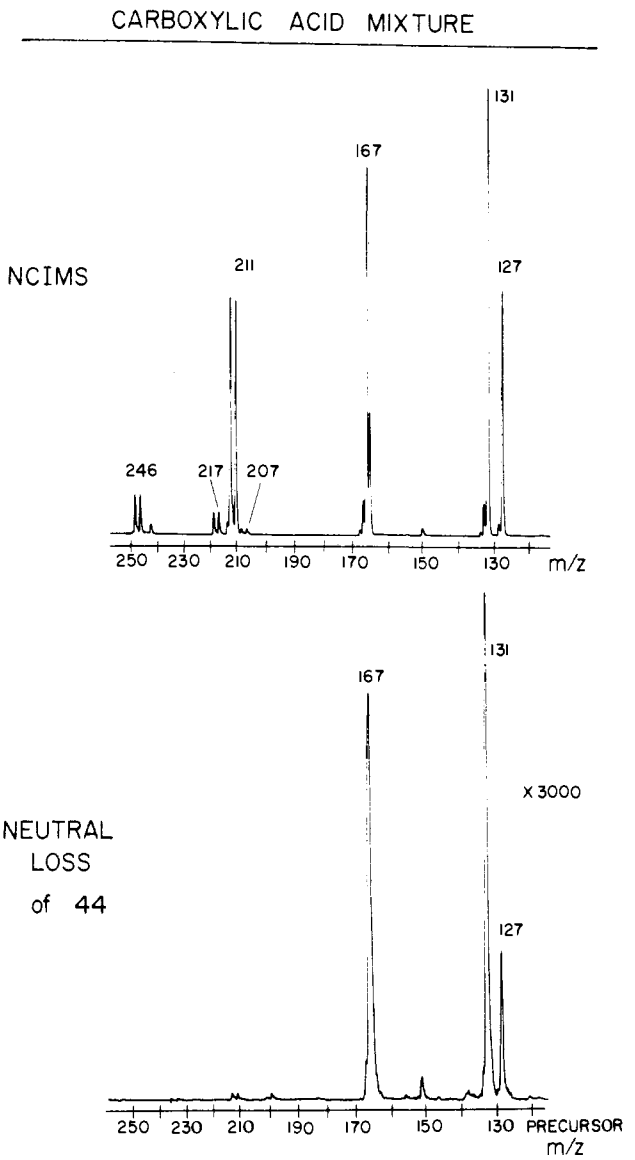

Figure 1. Comparison of the chemical ionization mass spectrum (CIMS) (isobutane, negative ions) with a scan which selects ions which undergo the reaction $m_1^- \rightarrow m_2^- + 44$. The sample consisted of a mixture containing barbituric acid ($(M - H)^-$ 127), glutaric acid ($(M - H)^-$ 131), and *p*-nitrobenzoic acid ($M^{-\cdot}$ 167).

The experiment consists of operating a dual analyzer mass spectrometer—in our work a reversed sector instrument, magnetic sector followed by electric sector—under computer control so that the two sectors are scanned in concert. In a typical analysis two spectra are acquired. The first is a normal mass spectrum of the mixture. The second, a selected fragment scan, employs active computer monitoring and control of the instrument. In the selected fragment scan mode the computer monitors the magnetic field as it is scanned, calculates the mass of the ion being transmitted by the magnet, and continuously sets the electric sector voltage to pass the appropriate m_2^+. Either m_2^+ can be held constant (selected fragment ion)[10] or m_3 can be held constant, $m_2^+ = m_1^+ -$ constant (selected *neutral* loss).

Mass spectra are most easily interpreted by examination of the neutrals lost from the molecular ion or quasi-molecular ion ($(M + H)^+$, $(M - H)^-$, etc.), hence the usefulness of the present method of scanning at fixed m_3 in the identification of functional groups. Figure 2 shows a neutral loss scan for another mixture containing carboxylic acids. Note that, in both the negative (Figure 1) and the positive ion spectra (Figure 2),

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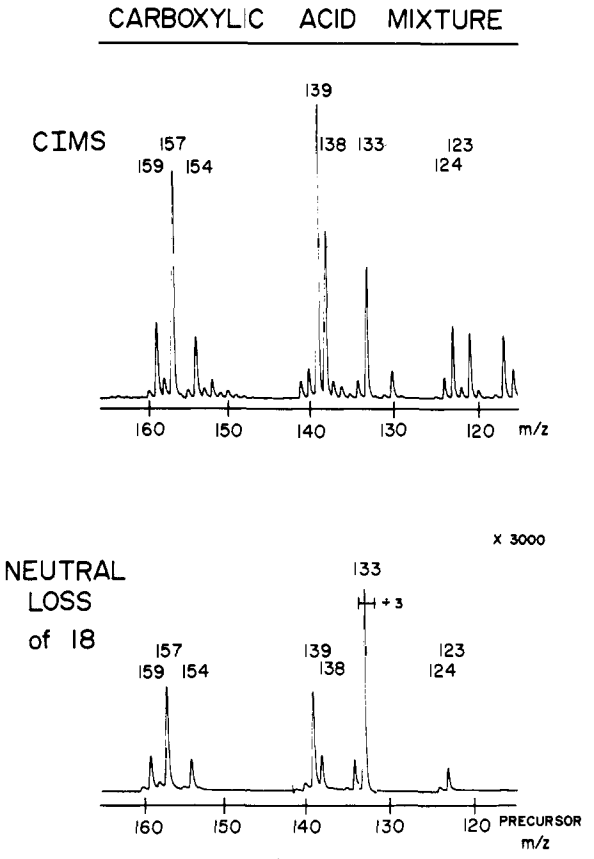

Figure 2. Comparison of the CIMS (isobutane, positive ions) with a scan which selects ions which undergo the collision-induced reaction $m_1^+ \rightarrow m_2^+ + 18$. The sample consisted of a mixture of benzoic acid (MH^+ 123), *m*-benzoic acid-*d* (MH^+ 124), glutaric acid (MH^+ 133), 4-hydroxybenzoic acid (MH^+ 139), and *p*-chlorobenzoic acid (MH^+ 157, 159). The scan rate in the selected fragment scan was 1 s/amu.

the only ions which appear in the neutral loss scan are those due to individual carboxylic acids.

A particularly significant extension of the experiment utilizes a combination of chemical and physical methods in establishing the presence of particular classes of compounds and the molecular weights of individual members of each class. This is done by derivatizing the entire sample using a reagent which is both chemically selective for the class of compounds in question and which can be readily identified in a subsequent selected fragment scan by monitoring either a characteristic neutral loss or fragment ion. A sequential chemical and spectroscopic test is thus imposed and the selectivity of the analysis is greatly increased.

A complex mixture containing six alcohols and phenols as well as numerous aliphatic and aromatic hydrocarbons was chosen to test the principle of this combined chemical and physical screening procedure. The entire sample was treated with a trimethylsilylating reagent to form the trimethylsilyl (TMS) derivatives of those compounds bearing OH groups. The complexity of this mixture resulted in a peak at every mass in the CIMS. The OH functional group was nevertheless identified by a selected fragment scan obtained so that m_2^+, the *charged* fragment, is constant. This was done by selecting 73^+, a prominent fragment ion observed on collision-induced dissociation of TMS derivatives. The scan of the derivatized mixture for 73^+ gave prominent responses for all of the original alcohols and phenols.

Figure 3 illustrates another example of functional group recognition using derivatization and selected fragment scans. A mixture of substituted phenols, dinitrobenzene, anthracene, and other compounds was acylated with acetyl chloride in pyridine. The reaction mixture was introduced directly into the mass spectrometer and a scan made for all ions which undergo loss of a neutral fragment of mass 42. As is evident from the figure, all the derivatized phenols give significant responses. This experiment therefore provides a necessary but not suffi-

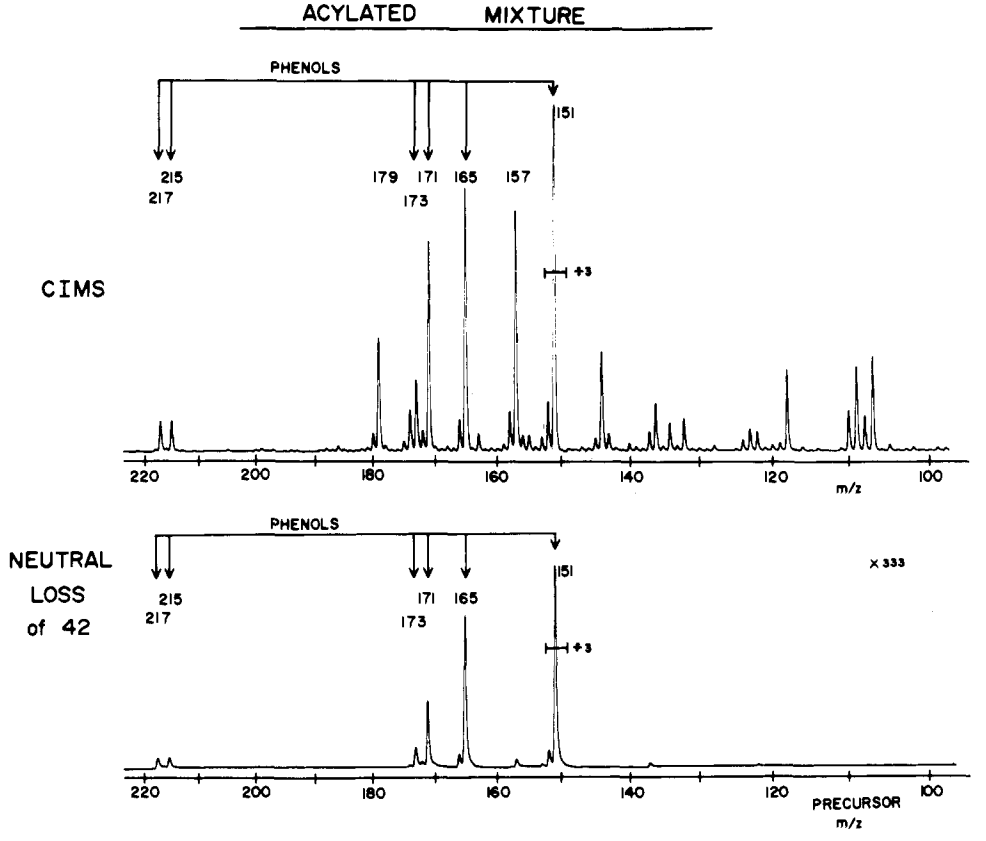

Figure 3. CIMS and selected fragment scans of an acetylated mixture including the phenols *o*-cresol (MH^+ 151), *p*-ethylphenol (MH^+ 165), *p*-chlorophenol (MH^+ 171, 173), and *p*-bromophenol (MH^+ 215, 217).

cient condition for establishing these constituents as phenols.

The procedures employed here are likely to simplify and enhance the use of mass spectrometry alone in the analysis of complex mixtures. Screening for particular functional groups seems to be as readily achieved as screening for individual compounds.[12] Most of all, the results demonstrate the exceptional versatility of mass spectrometers in chemical analysis.

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References and Notes

(1) R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973.
(2) (a) J. H. Beynon, R. G. Cooks, W. E. Baitinger, J. W. Amy, and T. Y. Ridley, *Anal. Chem.*, **45**, 1023A (1973); (b) T. Wachs, P. F. Bente, and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.*, *9*, 333 (1973).
(3) (a) M. Barber and R. M. Elliott, 12th Annual Conference on Mass Spectrometry and Allied Topics, ASTM Committee E-14, Montreal, 1964; (b) K. R. Jennings, *J. Chem. Phys.*, *43*, 4176 (1965); (c) J. H. Futrell, K. Lancaster, R. Ryan, and L. W. Sieck, *ibid.*, **43**, 1832 (1965).
(4) For a summary of scanning methods, see R. K. Boyd and J. H. Beynon, *Org. Mass Spectrom.*, **12**, 163 (1977).
(5) Comparable data can be obtained using an instrument of conventional geometry by linked scanning of two fields.[4]
(6) Preliminary results appear in R. W. Kondrat, Ph.D. Thesis, Purdue University, 1978, p 108. Since then, a paper describing the concept of selected fragment scans has appeared: M. J. Lacey and C. G. MacDonald, *Anal. Chem.*, **51**, 691 (1979). A parallel investigation using linked scanning of analyzing fields in an instrument of conventional geometry is underway: W. F. Haddon, *Org. Mass Spectrom.*, in press.
(7) The MIKES procedure is a particular example of a general approach[8] to mixture analysis which has been termed MS/MS (mass spectrometry/mass spectrometry).
(8) (a) T. L. Kruger, J. F. Litton, R. W. Kondrat, and R. G. Cooks, *Anal. Chem.*, **48**, 2113 (1976); (b) K. Levsen and H. R. Schulten, *Biomed. Mass Spectrom.*, **3**, 137 (1976); (c) J. H. McReynolds and M. Anbar, *Int. J. Mass Spectrom. Ion Phys.*, **24**, 37 (1977); (d) R. W. Kondrat and R. G. Cooks, *Anal. Chem.*, **50**, 81A (1978); (e) F. W. McLafferty and F. M. Brockhoff, *ibid.*, **50**, 69 (1978); (f) R. A. Yost, C. G. Enke, D. C. McGilvery, D. Smith, and J. D. Morrison, *Int. J. Mass Spectrom. Ion Phys.*, **30**, 127 (1979).
(9) G. A. McClusky, R. W. Kondrat, and R. G. Cooks, *J. Am. Chem. Soc.*, **100**, 6045 (1978).
(10) This result can also be obtained by scanning the accelerating voltage—a procedure which has seen some use in mixture analysis.[11]
(11) E. J. Gallegos, *Anal. Chem.*, **48**, 1348 (1976).
(12) (a) R. W. Kondrat, R. G. Cooks, and J. L. McLaughlin, *Science*, **199**, 1978 (1978); (b) A. Schoen, R. G. Cooks, and J. L. Wiebers, *ibid.*, **203**, 1249 (1979).

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Table I. Results with Large-Crystal ZSM-5

	alkylation	disproportionation	thermodynamic equilibrium
temp, °C	500	550	
WHSV[b]	6.6	30	
feedstock	2:1 mol ratio of toluene/methanol	toluene	
conversion, wt %			
toluene	39	13.2	
methanol	99		
product distribution,[c] wt %			
C_1–C_5	2.6	<0.1	
benzene	1.9	5.5	
toluene	54.0	86.8	
xylenes			
para	17.9	2.6	
meta	14.0	3.5	
ortho	7.0	1.4	
others	3.3	0.1	
% xylenes			
para	46	35	23
meta	36	46	51
ortho	18	19	26

[a] Weight hourly space velocity, (g of feed)/(g of catalyst) h^{-1}. [b] Organic phase.

Table II. Results with Chemically Modified ZSM-5

modification element	P	Mg
temp, °C	600	550
WHSV[a]	10	3.5
feedstock	2:1 mol ratio of toluene/methanol	toluene
conversion, wt %		
toluene	21	10.9
methanol	92	
product distribution,[b] wt %		
C_6^-	1.7	0
benzene	0.1	4.9
toluene	74.1	89.2
xylene		
para	20.7	5.2
meta	0.4	0.6
ortho	0.2	0.1
others	2.2	
% xylene		
para	97	88
meta	2	10
ortho	1	2

[a] See footnote *a*, Table I. [b] Organic phase.

Para-Directed Aromatic Reactions over Shape-Selective Molecular Sieve Zeolite Catalysts

Sir:

We have found that it is possible to alkylate or disproportionate certain monosubstituted benzene compounds to achieve nearly 100% selectivity to para-disubstituted derivatives with the molecular sieve zeolite catalyst ZSM-5[1,2] by modification of the latter with certain chemical reagents. An example is the alkylation of toluene with methanol to give primarily *p*-xylene and water. Toluene was also disproportionated to give *p*-xylene and benzene. This is in sharp contrast to results obtained with a variety of Friedel-Crafts catalysts and other solid acidic catalysts, including silica-alumina and zeolites where initial ortho-para substitution was observed, and where some subsequent isomerization usually occurred under the conditions of reaction to give a mixture of all isomers.[3-5]

Chemical reactions catalyzed by crystalline zeolites occur primarily within the catalysts' internal pore structure, which has precise dimensions characteristic of the individual zeolite species. By selection among the different zeolite species available, a variety of different pore and channel sizes are available. The interconnected channels formed by ten-membered rings of oxygen, such as in ZSM-5,[2] are especially interesting because certain benzene derivatives fit rather closely, are able to diffuse into the pores, reach a catalytic site, and undergo a reaction and the product may diffuse out. Other compounds or isomers may be too large to be formed easily or may diffuse out at greatly reduced rates.

When methanol is reacted over ZSM-5,[6,7] a hydrocarbon product mixture containing aromatic and aliphatic components is produced, the boiling range of which ends abruptly at compounds possessing ~10 carbon atoms. This molecular weight limitation is a result of the reactions occurring in a confined

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