

Early Gas Chromatography/Mass Spectrometry

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In December 1955 or thereabouts, the authors coupled a homemade gas chromatograph to a research time-of-flight mass spectrometer constructed by W. C. Wiley, I. H. McLaren, and D. B. Harrington. This unique gas chromatography/mass spectrometry (GC/MS) instrument generated mass spectra at a 10-kHz rate for display on an oscilloscope; eluted gas chromatographic components, such as methanol, acetone, benzene, toluene, and carbon tetrachloride, could be visually identified immediately from the oscilloscope display. Many years of further research and development in many laboratories worldwide were necessary, however, to make continuous on-line GC/MS the uniquely valuable analytical tool that it is today. (*J Am Soc Mass Spectrom* 1993, 4, 367-371)

For the first decade after its introduction in 1942, the commercial mass spectrometer was used almost entirely for quantitative analysis of volatile hydrocarbons [1-3]. Reports of the mass spectrometry of other compound types were appearing [4-11] in the early 1950s when the authors joined the Spectroscopy Laboratory at the Dow Chemical Company. Here a vigorous research program had already developed important instrumental analytical techniques, such as x-ray diffraction, atomic emission, and infrared absorption spectroscopy, applicable to a wide variety of the company's problems. Its Director, Norman Wright [12], and the Group Leader, Jason Saunderson, had also encouraged similar mass spectrometry research with two Westinghouse mass spectrometers partially constructed by Victor Caldecourt [13]; these instruments and a CEC 21-103B were applied to a variety of chemical problems [14-17].

Early Gas Chromatography

In 1954, Steve DalNogare of Dupont and H. N. Wilson of ICI (Billingham, UK) introduced [18] one of the authors (F.W.M.) to "vapor-phase" (now "gas") chromatography (GC) [19], and the other author (R.S.G.) constructed literally hundreds of these instruments for various Dow applications before more desirable instruments were available commercially. The 1955 homemade gas chromatograph used approximately 12 ft. of 1/4-in. stainless steel or copper tubing containing coated, crushed firebrick wound into a spiral and fitted

into a 1-gal Dewar flask filled with silicone fluid heated with a Calrod immersion heater (Figure 1) [16]. The Gow-Mac instrument company designed for us a stainless-steel thermal conductivity cell detector with seals capable of operation at 300 °C.

Why Gas Chromatography/Mass Spectrometry?

We have often been asked why we next wanted to obtain mass spectra directly from the GC effluent. Of course GC proved valuable immediately for company problems with unknown mixtures too complex for direct analysis by mass spectrometry. However, indicating the number and even the concentration of these components often did not solve the problem; one or more components required identification, but these were in such small amounts that transfer to a suitable instrument was difficult. A number of laboratories developed techniques in which a detected GC fraction was trapped cryogenically for scanning by mass spectrometry while the GC flow was stopped [20, 21].

As a second incentive, in 1955 we heard from our Michigan neighbors Bill Wiley and Dan Harrington of a new mass spectrometer constructed at their Bendix laboratory based on the time-of-flight (TOF) principle. This instrument measures spectra at a 10-kHz rate for oscilloscopic display, with unit mass resolution up to m/z 150 [22, 23]. They had not obtained spectra of organic compounds but, knowing our interests, challenged us to find ways to utilize these exciting capabilities.

Finally, it soon became obvious that the much less expensive, simpler GC could be an overwhelming competitor of mass spectrometry in analytical applica-

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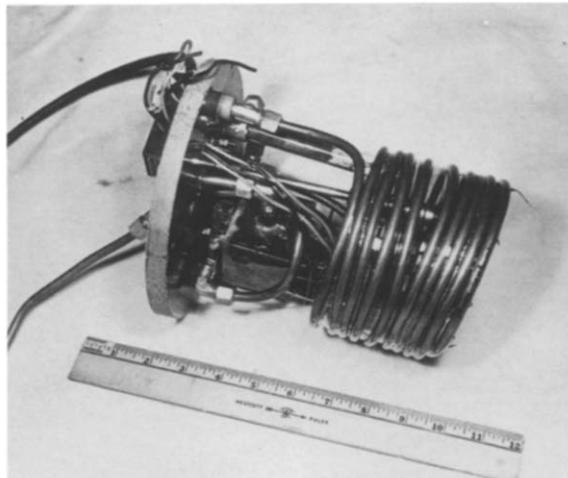


Figure 1. Gas chromatograph constructed at Dow in 1955.

tions—if you can't beat 'em, join 'em. The great potential of GC was obvious to many analytical chemists who had never heard of mass spectrometry, and this prediction has been amply borne out by the widespread GC applications today. In consolation, although GC annual sales are now far greater than those of mass spectrometry, gas chromatography/mass spectrometry (GC/MS) sales are also far greater than those of all other types of mass spectrometry systems combined.

On-Line Identification by Mass Spectrometry of Gas Chromatography Separated Compounds

To implement GC/MS, a small portion (< 1%) of GC effluent was split to the mass spectrometer through a Nupro metering valve (Figure 2). Several instruments, including the Bennett radiofrequency, omegatron, and GE monopole, were considered. Attempts to modify

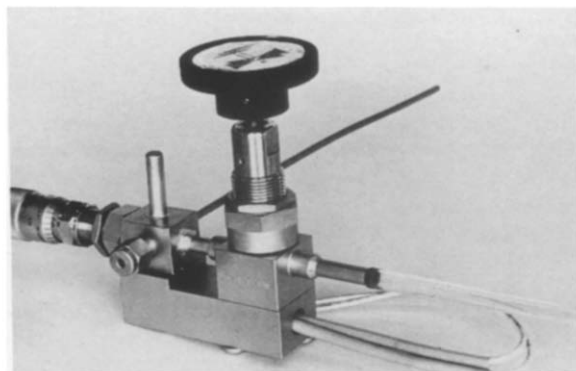


Figure 2. Modified Nupro metering valve for splitting the GC effluent (front) to the mass spectrometer (right), with the main flow to the thermal conductivity detector (rear).

our magnetic sector instruments for sufficiently rapid scanning produced badly distorted spectra of poor mass resolution, even over limited mass ranges. In 1957, Holmes and Morrell [24] reported results from a similar conventional system using a CEC 21-103B mass spectrometer capable of scanning from m/z 28 to 44 every 15 s, or m/z 12–1000 in 60 s; their single illustration is a spectrum of m/z 35–50 from butane.

In our discussion with Wiley and Harrington about the TOF instrument, they generously invited us to drive down to the Bendix Research Laboratory in Southfield, Michigan, despite the fact that only their original research instrument was yet in operation. Unfortunately, the date of this visit is not certain.¹ We remember that it was winter, after the date for submitting abstracts for the Spring 1956 American Chemical Society meeting; we first reported GC/MS [25] at this meeting, as described briefly in 1956 [23] and 1957 [17] but not in full until 1959 [26]. Besides the homemade gas chromatograph and interface, we took to Detroit samples of common organic compounds and introduction hypodermic syringes. In preparation for our visit, Harrington practiced photographing repeated series of instrument background spectra from the oscilloscope with a Polaroid camera. The Bendix instrument² had no sample inlet system; luckily, there was a "back-to-air" vent valve located near the ion source region to which we connected the interface tube from the gas chromatograph.

All of us still remember the tremendously exciting next moments as we crowded around the instrument [27], but Harrington's words tell it best²:

Roland injected his sample and then glued his eyes to the auxiliary oscilloscope readout. As each separated compound showed its mass spectrum, Roland told me when to take a photograph of the mass spectrum using a Polaroid camera attached to the TOF's primary oscilloscope readout. How excited and pleased Bill and I and the other Bendix folks were when we heard Roland exclaim over and over how similar the oscilloscope spectra were to the magnetic mass spectrometer spectra with which he was familiar.

As each eluted compound reached the mass spectrometer, the spectral peaks would rise up together out of the baseline; the sight of the m/z 117/119/121 peaks of carbon tetrachloride growing up in their familiar isotopic ratio is still a vivid memory.³ F.W.M. remembers feeling disadvantaged that he had to look over

¹ All Dow research records before 1957 have now been destroyed; the most probable date of this visit is December 1955.

² D. B. Harrington, personal communications, May 25 and June 6, 1992; that of January 8, 1993 describes the TOF instrument as "the old chewing-gum and bailing-wire beast."

³ Perhaps F.W.M.'s memory on this is "sharpened" because of R.S.G.'s favorite TOF/MS demonstration for lab visitors. He would put a finger on the mass spectrometer inlet and pull a vacuum on his skin; he would then dip a finger of his other hand into CCl_4 , with its mass spectrum rising up on the oscilloscope in 20–30 s.

R.S.G.'s shoulder to hear him shout words like "methanol," "acetone," "benzone," and "toluene" while F.W.M. was still straining to see peaks only partly out of the baseline. We really did not know what kind of mass spectra the TOF instrument would produce, and it was tremendously gratifying that the spectra looked just like old friends despite the fact that they were generated in a tiny fraction of the time of our usual 10-30 min for pen recorder and oscillographic scans; an example [26] is shown in Table 1.

Gas Chromatography/Mass Spectrometry Development at Dow

On their return to Midland, the excited authors persuaded Dow to order a TOF mass spectrometry instrument (price \$12,000!), which was delivered the following winter (Figure 3). This was a record production time because two other units were shipped first to DuPont, apparently for process monitoring [27]. Further GC/MS research in Midland using this commercial Bendix instrument was largely due to R.S.G. because F.W.M. transferred in June 1956 to Dow's new Eastern Research Laboratory near Boston. The earliest spectra¹ that we have located (Polaroid film dated April 1957) are from this new instrument (Figure 4) and should be relatively similar to those taken first at Bendix on the research TOF instrument. Our mass spectrometrists readers should try duplicating the "instant" R.S.G. identification that the TOF oscilloscope display made possible.

This GC/MS instrument was found useful immediately in a wide variety of important Dow problems. The high use demand led to a number of improvements, such as using one Polaroid film to record several separate mass spectra or expanded versions of a single spectrum (Figure 5) by racking the camera body manually in a vertical direction. Another improvement made possible spectrum scanning by gating electrodes that allowed only a narrow range of ion flight times to reach the multiplier at any moment [23]; by lengthening the time delay, the entire spectrum could be

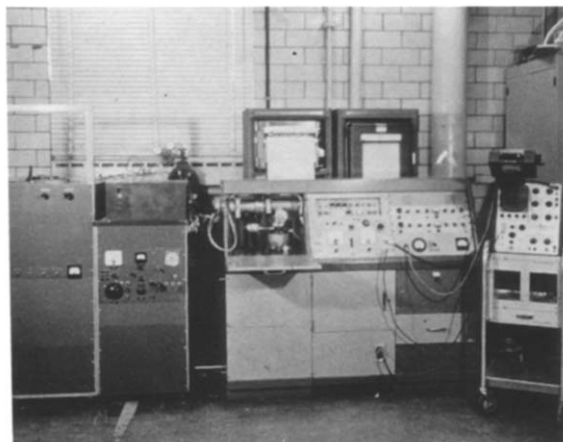


Figure 3. Dow gas chromatograph and Bendix TOF mass spectrometer in the Dow Spectroscopy Laboratory, 1957.

recorded on a strip-chart recorder (Figure 3) or, later, on a Minneapolis-Honeywell Visicorder in times as short as 1 s. In a modification, this scan technique was used only on every other mass spectrum (2-kHz rate), with the total ion abundance monitored on the intervening spectra. The Visicorder output could then show separate displays of the scanned spectrum and the total ion current as a function of time (Figure 6), yielding a quantitative profile of the eluting GC peak as well as its mass spectrum.

The orders-of-magnitude faster rate of generating spectra placed a great premium on "eyeball" interpretation and even led to the development of an early

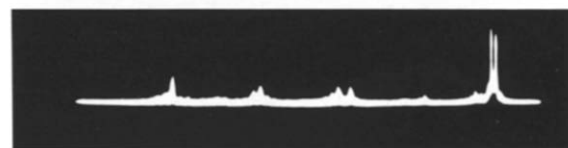
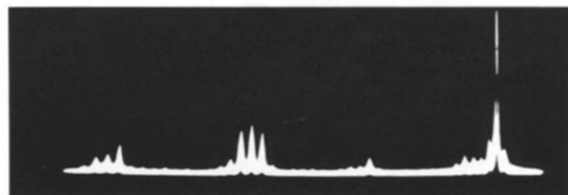
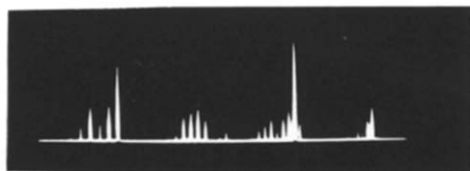


Figure 4. Mass spectra recorded on Polaroid film of eluted GC fractions. Top to bottom: acetone (peaks m/z 14-58), benzene (peaks m/z 36-79), and toluene (peaks m/z 27-92).

Table 1. Mass spectra of vinyl chloride

m/z	CEC 21-103	Time of flight
12	4.7	5
25	17.4	18
26	43.3	42
27	132	140
35	9.0	10
47	4.7	5
48	2.1	2
59	1.9	2
60	6.3	6
61	9.0	9
62	100	100
63	4.8	5
64	31.6	32
65	0.7	< 1

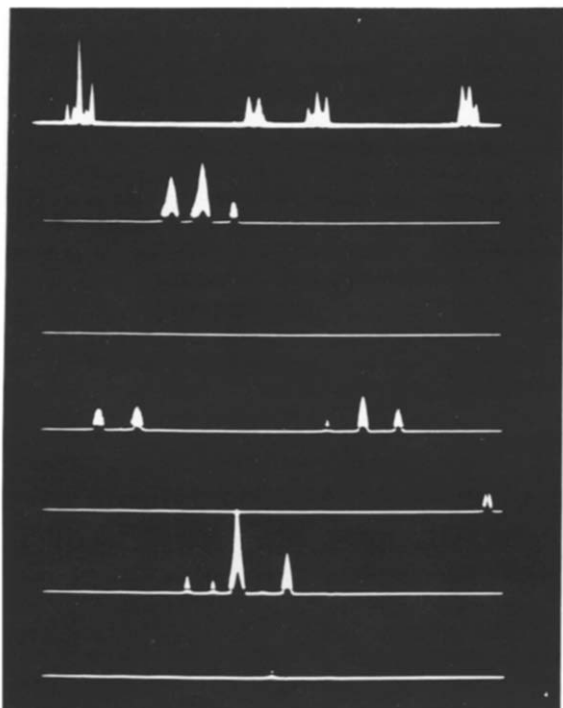


Figure 5. Mass spectrum of eluted GC fraction (bromochloromethane). Top to bottom: m/z 42-139, 120-149, 97-123, 76-100, 56-80, 42-59, and 27-43.

"computerized" identification system [28] modeled after one developed for infrared spectra [12]. This used an IBM collator to search out 4000 spectra database on 72,000 Hollerith punchcards. A further vivid memory illustrating this data problem was a visit by Herb Dutton of the US Northern Regional Research Laboratory bringing fatty acid mixtures important to their lipid research. As each peak came off the gas chromatograph, the Visicorder button was pushed to shoot out a few feet of paper with the corresponding mass spectrum. At the end of a couple of hours, Dutton had scores of spectra to take home for interpretation, a job of many days without instrument mass assignment.

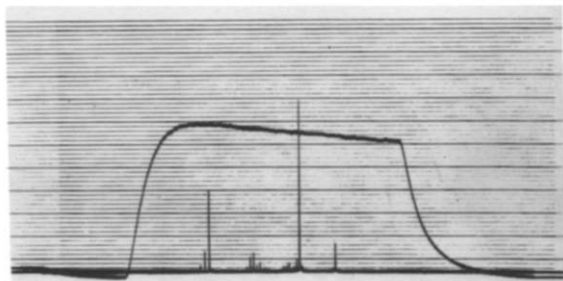


Figure 6. Visicorder mass spectrum of GC-eluted acetone fraction recorded simultaneously with the total ion current from corresponding GC peak, with ~ 2 s.

Despite this, his laboratory did purchase a TOF instrument [29].

Further Gas Chromatography/Mass Spectrometry Development

In the next decade, many scientists in many laboratories realized the great potential of GC/MS [29-34]. Especially critical for its development were methods for GC carrier gas removal, such as effusion separators (Watson-Biemann), jet separators (Ryhage-Stenhagen), and semipermeable membranes (Llewellyn-Littlejohn). Computer acquisition, reduction, and interpretation of spectra have also become far more efficient with the corresponding dramatic improvements in computer technology, and the sophisticated engineering of "benchtop" GC/MS instruments is also a key to their user-friendliness and lower price, making them a convenient tool in many modern laboratories and plants [35]. Although these instruments can even give GC peak identifications in real time by matching the unknown mass spectrum against a reference file [36], the 10-kHz scan rate of the 1955 Bendix TOF mass spectrometer is still far faster than that of any modern commercial GC/MS instrument. Because it was many years before any other mass spectrometer could scan a complete spectrum in the few seconds' width of an eluting GC peak, it would appear that this Dow/Bendix effort was the pioneering experiment in developing GC/MS as the unique analytical tool that it is today.

Acknowledgments

None of this work would have been possible without the pioneering Bendix TOF instrumentation and its inspired operation; of that group, Bill Wiley and Dan Harrington are the ones best known to the authors, but others surely deserve credit. The authors also received a great deal of advice and help from many Dow people, including Bob Abernathy, Sam Adler, Vic Caldecourt, Eugene Camehl, Bill Felmler, Joanne Gilpin, Mynard Haming, Ray Narlock, Coyt Pratt, Evan Ruby, Jason Saunderson, Bill Scott, Jim Tou, Herb Woodcock, and Norman Wright. Our memories were also greatly aided by John Beynon, A. J. "Jack" Sharkey, Sy Meyerson, Ragnar Ryhage, Herb Dutton, and Harro Limbo (Polaroid Corp.). Information gathering for this report was supported, in part, by National Institutes of Health, grant GM16609.

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