By proper preparation and calibration of standards, the procedure can be expanded to handle items other than 1-gallon cans. Known quantities of ^{238}Pu were added to three types of glove box exhaust filters (box filters 20.3 cm × 20.3 cm × 15.2 cm and 20.3 cm × 20.3 cm × 7.6 cm, and cannister filters 16.8-cm diameter and 28.6 cm long). Values for *F* were determined for each type of filter and the filters are now assayed routinely with the same accuracy as the waste cans.

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Perfluoroalkyl-*s*-Triazines as Mass Calibration Standards for Time-of-Flight Spectrometry

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IN ORDER to determine the mass of an ion produced in a mass spectrometer, it is often necessary to introduce along with the sample a calibration standard which gives reference ions of known mass. Both the method of calculation and the choice of standard depend upon the nature of the spectrometer used. Although this variability in requirements has been observed by mass spectrometrists possessing the necessarily varied experience, and although valuable bits of information are exchanged at users' conferences and transmitted somewhat haphazardly through the medium of the manufacturers' service engineers, the inadequacy of published information is still an unnecessary handicap to the operator who sets out in the traditional industrial fashion to teach himself the use of the instrument.

The following discussion of mass spectrometric calibration problems is based mainly upon the use of the Bendix time-of-flight mass spectrometer in this laboratory. The operation of this system is compared with that of the Consolidated Electrodynamics Model 21-1108 high resolution instrument, complete with the 21-087 digital recording system for photographic plate data and with the associated computer programs (*1*). The use of internal standards (standards admitted simultaneously with the sample) is a common procedure for both instruments.

Both the similarities and the differences of the low resolution and high resolution problems are worthy of mention. In the time-of-flight instrument, mass standards are used to get nominal unit mass values. In the high resolution double focusing mass spectrometer, standards are required for the achievement of satisfactory accuracy in terms of a few parts per million of mass. The approximate but not exactly linear variation of the square root of mass with distance is common to both the high resolution photographic plate and the time-of-flight recorder chart. At this point, an important difference must be noted. For the high resolution spectrometer, the best standard found for the range below 600 mass units appears to be a suitable grade of "perfluorokerosene" or "perfluoroalkane," of which several, with different boiling ranges, are commercially available. Their peaks are numerous, are closely spaced except for a troublesome gap between *m/e* 31 and *m/e* 50, and in the high resolution spectrometer are sufficiently widely resolved from those of the usual carbon–hydrogen–nitrogen–oxygen compounds as to cause no confusion. Because the experimental data are read from the plate by a largely automatic system, digitized, recorded on magnetic tape, and processed by a computer, the operator is not much burdened by the details of the arithmetic.

In the time-of-flight instrument, on the other hand, the fluorocarbon peaks are not resolved from sample peaks occurring at the same mass values. Because of this overlap, and because the higher mass peaks of perfluorokerosene are of quite low intensity as compared with such light ones as CF_3^+ (which tend to saturate both the multiplier and the analog unit), perfluorokerosene is a poor standard for time-of-flight spectrometry. Here, peaks of low intensity tend to be poorly shaped, reflecting the random fluctuations of ion statistics, and are frequently unusable for purposes of calibration.

In addition to the usual requirements of sufficient volatility, stability, and availability, it is desirable that the time-of-flight mass standard have a simple spectrum, in the sense that it should consist of a rather small number of relatively intense peaks. Because the peaks of low intensity are both inferior for calibration and troublesome in their overlapping of sample peaks, it is desirable that they be as few as possible.

The writers observed years ago that the attempt to reduce the total air leakage rate below a certain reasonable level was, except for analyses of gaseous samples, not particularly desirable in a time-of-flight mass spectrometer that was used very successfully to carry out both occasional research and a large and highly varied service program for other research groups. The air peaks provided an easily recognizable calibration of the lower mass range, as has been reported by Biemann (*2*). Beginning with two of them, the constant *k* in the usual square root expression, Equation 1, was determined, and the same equation in the form of Equation 2 was used to proceed point by point along the mass scale, using pairs of the identified sample peaks for successive redeterminations of

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(1) J. M. Ruth, U. S. Dept. of Agriculture, Beltsville, Md. 20705, private communication, 1968.

(2) K. Biemann, "Mass Spectroscopy-Organic Chemical Applications," McGraw-Hill, New York, 1962, pp 38–9.

the constant k whenever the calculated nominal mass values drifted off by two or three tenths of a mass unit, until perhaps

$$k = \frac{\sqrt{M_1} - \sqrt{M_0}}{D_1 - D_0} \tag{1}$$

$$M = [\sqrt{M_0} + k(D - D_0)]^2 \tag{2}$$

the occurrence of an inconveniently long gap in the sequence of observed masses made the use of other identifiable standard peaks necessary in the higher mass range. Here, M represents the m/e value of a peak, rounded usually to its nominal integral value, although it is sometimes preferable to carry one decimal place when using fluorinated or iodinated standards in the higher mass range, and D is the position of the peak center as measured from an arbitrary origin of the mass scale. This system of calculation, based upon the square root equation supplied by the manufacturer, was found superior to graphical methods of calibration. A good time-of-flight operator was able to work his way up the mass scale quite rapidly with a desk calculator. References in the literature (*2*, *3*) to the use of pump oil peaks for "counting" purposes record another effective mass standard.

It has been the custom in this laboratory to keep a small collection of mass standards, including both volatile liquids and a group of solids, mainly iodine compounds (*4*), which had been found to evaporate at suitable rates, some when placed in the direct inlet probe capillary and heated, and some when a crystal, such as one of iodoform, was placed without other confinement upon the large top of the vertically traveling probe and permitted to sublime from there. Among the most useful liquids were perfluorotributylamine and perfluorobutylfuran, called "FC-43" and "FC-75," respectively, and supplied by the Minnesota Mining and Manufacturing Co.

Tris(pentafluoroethyl)-*s*-triazine, one of a group of fluorochemicals whose mass spectra were reported by Hynes (*5*), was also frequently used. Because each of these three fluorine compounds (to say nothing of the iodine compounds) exhibited gaps of excessive length, it was common practice to get as much information as possible with the first one chosen, and then, if necessary, to rerun the sample with another standard. As noted above, perfluorokerosene was examined rather early, but was not found very useful at the time with that instrument. The tris(heptafluoro-*n*-propyl)-*s*-triazine was made later, in order to extend the range of m/e values, and finally a mixture of perfluoroalkyl-*s*-triazines was prepared to eliminate the long gaps in the spectra of the pure compounds. This mixture, whose preparation and mass spectrum are reported here, has been found to fulfill the requirements of a good general reference standard for the time-of-flight spectrometer out to m/e 585. This mass range is sufficient for a majority of the samples analyzed, but it could be extended by the addition of a heavier homolog to the mixture. The high resolution mass spectrum of tris(pentadecafluoroheptyl)-*s*-triazine has recently been reported (*6*) and a variety of perfluoroalkyl-*s*-triazines have recently become commercially available from Peninsular ChemResearch, Inc., Gainesville, Fla.

Table I. Mass Spectra of the Perfluoro-*s*-Triazines

	Relative ion abundance			
m/e	$C_3N_3F_3$[a]	$C_3N_3(CF_3)_3$	C_3N_3-$(C_2F_5)_3$	C_3N_3-$(C_3F_7)_3$
26	21.7	...	1.4	...
28	13.3	...	...	...
31	98.3	23.3	12.1	6.92
38	11.7	2.0	...	...
45	93.3	...	...	...
50	...	35.0	9.3	4.46
52	13.3	4.3	...	...
57	3.7	3.0	2.0	...
62	2.8	...	...	...
69	...	100.0	100.0	100.0
71	93.3	...	...	...
76	4.2	50.0	73.3	83.0
78	...	6.7	...	...
83	...	...	5.3	...
85	...	...	2.8	...
90	95.0	...	...	...
100	...	...	10.5	11.2
102	...	13.3	9.7	9.82
107	...	...	2.4	2.68
116	36.7	...	...	...
119	...	...	40.5	16.5
121	...	66.7	...	...
126	...	...	13.3	6.72
131	...	...	...	2.10
133	...	...	...	2.88
135	100.0	...	...	...
138	...	...	...	0.78
150	...	...	...	1.12
152	...	...	2.4	1.16
169	...	...	...	20.8
171	...	...	12.9	...
176	...	...	...	3.30
178	...	...	2.0	2.17
190	...	38.3	...	...
221	...	...	...	5.13
266	...	36.6	...	...
285	...	36.6	...	...
347	...	...	1.1	...
366	...	...	37.6	3.21
371	...	...	...	2.08
416	...	...	19.8	0.85
435	...	...	14.9	...
466	...	...	...	70.1
516	...	...	...	0.78
566	...	...	...	17.2
585	...	...	...	9.04

[a] This spectrum added as reference.

EXPERIMENTAL

Synthesis of Triazines. The symmetrical perfluoroalkyl-*s*-triazines were prepared according to the method of Bissell and Spenger (*7*) with equal molar quantities of hydrogen chloride and nitrile at ambient temperature. Their boiling points agreed with literature values (*8*) and their purities were established by gas chromatography and infrared analysis (*9*). The unsymmetrical mixtures were prepared by the same method with equal molar amounts of hydrogen chloride and the two requisite nitriles. The reaction product obtained from CF_3CN and C_2F_5CN were distilled to yield a principal fraction boiling from 107–118 °C. This material, Mixture 1, was used without further rectification. The product of the reaction of C_2F_5CN and n-C_3F_7CN was obtained in lower

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(3) R. W. Kiser, "Introduction to Mass Spectroscopy and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 209.

(4) J. M. Ruth, U. S. Dept. of Agriculture, Beltsville, Md. 20705, unpublished data, 1968.

(5) J. B. Hynes, Ph.D. Thesis, Duke University, Durham, N. C., 1961.

(6) T. Aczel, ANAL. CHEM., **40**, 1917 (1968).

(7) E. R. Bissell and R. E. Spenger, *J. Org. Chem.*, **24**, 1147 (1959).

(8) W. L. Reilley and H. C. Brown, *ibid.*, **22**, 698 (1957).

(9) J. W. Dawson, J. B. Hynes, K. Niedenzu, and W. Sawodny, *Spectrochim. Acta*, **23A**, 1211 (1967).

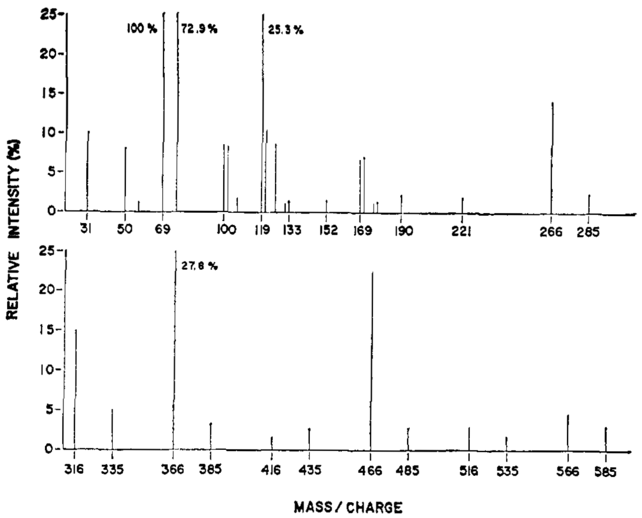

Figure 1. Mass spectrum of proposed calibration standard mixture of perfluoroalkyl-*s*-triazines

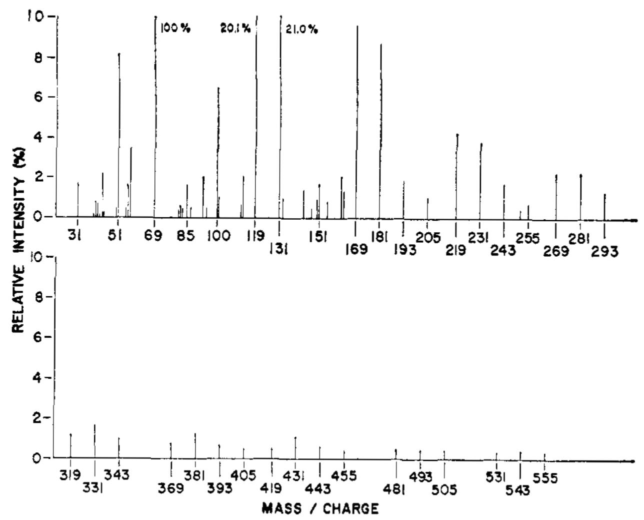

Figure 2. Mass spectrum of perfluoroalkane 225

Table II. Mass Spectra of Unsymmetrically Substituted Perfluoro-*s*-Triazine Mixtures

	Relative ion abundance	
m/e	CF_3CN + C_2F_5CN	C_2F_5CN + C_3F_7CN
31	10.3	10.7
50	8.87	7.39
57	0.83	1.63
69	100.0	100.0
76	53.4	100.0
100	3.64	13.1
102	5.23	11.1
107	...	2.45
119	17.9	41.6
121	20.4	...
126	4.46	15.9
131	...	1.63
133	...	2.20
152	0.58	2.16
169	...	9.14
171	6.14	10.2
176	...	1.51
178	...	1.96
221	...	1.71
266	30.3	...
285	4.13	...
316	32.0	...
335	12.2	...
366	16.0	53.1
385	6.58	...
416	2.29	40.0
435	1.79	4.69
466	...	19.2
485	...	8.65
516	...	8.53
535	...	4.82
566	...	1.02
585	...	0.49

conversion, approximately 50%. The crude trimeric mixture was washed with water, dried, and distilled to yield a central fraction, Mixture 2, boiling from 131 to 151 °C, which consisted principally of the mixed trimers $(C_2F_5CN)_2$-*n*-C_3F_7CN and $C_2F_5CN(n\text{-}C_3F_7CN)_2$. Mixture 3 contains Mixture 1, Mixture 2, and the tris(heptafluoro-*n*-propyl)-*s*-triazine) in the ratio 2:2:1.

Mass Spectra. The mass spectra of the triazines were determined by direct injection into the heated inlet system of the Bendix Model 14 time-of-flight mass spectrometer.

RESULTS

The mass spectra of the symmetrical compounds are tabulated in Table I while the spectra of the two mixtures of unsymmetrically substituted triazines are given in Table II. No attempt has been made to assign formulas to all of the ion species; however, the highest *m/e* peaks for the pure materials are the parent ions and in the mixtures these are the parent ions of the compound of greatest molecular weight.

The two mixtures of unsymmetrical triazines also contain the two symmetrical compounds; however, the principal components are the two unsymmetrical compounds in their respective mixtures.

The spectrum in Figure 1 is that of a proposed mass calibration standard containing both unsymmetrically substituted *s*-triazine mixtures and the tris(heptafluoro-*n*-propyl)-*s*-triazine compounds in the ratio 2:2:1. This standard mixture gives well spaced masses from *m/e* 250 to 585 with a reasonable range of intensities. No unknown mass peak in this range could be more than 16 mass units from a standard peak. The spectrum of perfluoroalkane, 225, in Figure 2 in contrast to that of the above proposed standard exhibits mass peaks with much lower relative intensities in the higher mass range where calibration becomes more difficult for time-of-flight data.

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