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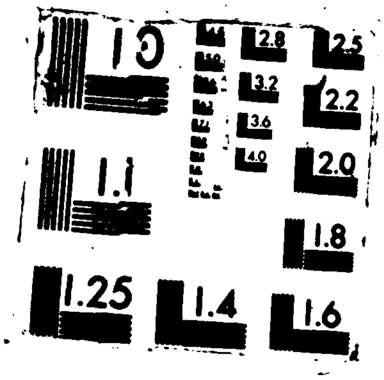
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6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION

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8a. NAME OF FUNDING/SPONSORING ORGANIZATION
O.N.R.

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
800 N. Quincy St.
Arlington, VA 22217

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO

11. TITLE *(Include Security Classification)*
Fourier Transform Ion Cyclotron Resonance Mass Spectrometry at Low Magnetic Fields: Several Figures of Merit

12. PERSONAL AUTHOR(S)
B. A. Hearn, G. Baykut and J. R. Eyler

13a. TYPE OF REPORT
Technical

13b. TIME COVERED
FROM 1/85 TO 9/86

14. DATE OF REPORT *(Year, Month, Day)*
1987, July 29

15. PAGE COUNT
21

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Fourier Transform, Ion Cyclotron, Mass Spectrometry; Instrumentation, Miniaturization .

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

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21. ABSTRACT SECURITY CLASSIFICATION
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22c. OFFICE SYMBOL

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OFFICE OF NAVAL RESEARCH

Contract N00014-82-K-0509

R & T Code 413a001___01

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Task No. NR 051-820

TECHNICAL REPORT NO. 11

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by

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July 29, 1987

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Fourier Transform Ion Cyclotron Resonance Mass Spectrometry at Low Magnetic Fields: Several Figures of Merit

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ABSTRACT

A Fourier transform ion cyclotron resonance mass spectrometer based on a permanent magnet with a magnetic induction of 0.16 T with low homogeneity provided a precision of 3.2% (taken as the relative standard deviation of the hourly mean of three independent measurements) over a 5 hour period and a precision of 11.7% for daily measurements over a 10 day period. For the permanent magnet system, resolution values for perdeuterated benzene (m/z 84) for a given mass range and a given number of data points were similar to those measured for both an electromagnet (0.2 to 1.0 T) and a superconducting solenoid (3.0 T). Signal-to-noise ratios for perdeuterated benzene obtained with the three different magnets were also measured.

INTRODUCTION

The unparalleled mass resolution (1) and extremely accurate mass measurement (2,3) made possible by Fourier transform ion cyclotron resonance mass spectrometry (FTICR) reflect the current trend in commercial instrumentation development. Along with the rising performance of FTICR, instrument complexity is also increasing, which in many cases means a more expensive instrument. Incorporation of this promising type of mass spectrometry into the analytical chemistry community has been limited, in part, by budgetary restrictions. Widespread acceptance of FTICR techniques for routine analysis in multifunctional analytical chemistry laboratories will only follow a significant increase in their information/cost ratio. However, the cost factor in the information/cost ratio for FTICR has, for the most part, been ignored in instrumentation development to date. This study deals with one aspect of this factor: can a FTICR mass spectrometer based on an inexpensive low field permanent magnet be used to provide useful information to the analytical chemist?

Three aspects of low magnetic field FTICR were investigated: precision, resolution, and signal-to-noise ratio (S/N). In 1976, Comisarow and Marshall showed that in the low pressure limit the resolution for a magnitude-mode line for an ion of mass m in FTICR is given by (4):

$$m/\Delta m_{50\%} = qBt/7.86 \times 10^{-4} m \qquad (1)$$

where $\Delta m_{50\%}$ is the full peak width at half height, q is the charge of the ion, B is the magnetic induction, and t is the acquisition time of the signal. From this general equation for resolution of a FTICR signal, another expression for the resolution at low pressures can be derived (4):

$$m/\Delta m_{50\%} = NP\ m_{min}/2.413\ m \qquad (2)$$

where NP is the number of points acquired in the time domain spectrum, m_{min} is the minimum mass (which determines the maximum digitization frequency), and the other terms are as given above. This equation shows that, for low pressures, the resolution of a magnitude-mode signal in FTICR with a given mass range is independent of the magnetic induction. The requirement for this resolution is that the signal persist for the entire digitization time. It should be emphasized here that to achieve a given resolution value, longer digitization times are required in the case of lower magnetic fields. A general equation for S/N expected for an FTICR signal is (5)

$$S/N = N\ q^2 rBR^{1/2}/2md(2kT\Delta f)^{1/2} \qquad (3)$$

where N is the number of ions of mass m which have been excited to an orbital radius r, R is the effective resistance of the detection circuit, d is the cell plate spacing, k is the Boltzmann constant, T is the temperature, Δf is the detection bandwidth, and the other terms are as defined above. Thus S/N is predicted by this equation to be proportional to B, the magnetic induction.

EXPERIMENTAL SECTION

Mass spectrometric measurements were performed with a commercial Nicolet FT/MS-1000 Fourier transform mass spectrometer data console and associated electronics using an analyzer cell and vacuum chamber constructed at the University of Florida. The vacuum chamber dimensions were such that it would fit into either a modified permanent magnet or an electromagnet. The permanent magnet (0.16 T), from a Varian bench-top nuclear magnetic resonance spectrometer, had the pole faces removed from the 11 cm diameter poles to give a 4.6 cm gap which was large enough to accomodate the vacuum chamber. Over the central 2.5 cm volume of the permanent magnet, the magnetic induction varied by approximately 0.5%. The electromagnet, a 23 cm Varian electromagnet with a 5 cm gap and Fieldial regulated output, provided magnetic inductions from 0 to 1.4 T. For measurements at higher magnetic fields, the Oxford superconducting solenoid (3.0 T) from a commercial Nicolet FTICR system was used, along with the analyzer cell and vacuum chamber for the superconducting solenoid.

Operating conditions for wide-band spectra taken with the permanent magnet were as follows. A mixture with a total pressure of 2.3×10^{-7} torr was obtained in the vacuum system by introducing 1×10^{-7} torr helium, 1×10^{-7} torr air, and 3×10^{-8} torr H_2O into the vacuum system through leak valves. Indicated (but uncorrected) ionization gauge pressures are given here, which will be used throughout this paper. For absolute pressures, the response factor of the ionization gauge for different gases would have to be taken into account. Ions were produced by a beam of 30 eV electrons which gave a 900 nA emission current and were trapped in the analyzer cell by a 2.0 V trapping potential. The 5.0 ms electron beam was followed by excitation of the ions and a wide-band digitization of 8k data points at 5.32 MHz. The average of 1000 time domain signals was then zero filled once to give a total of 16k real data points and Fourier transformed to give the mass spectrum.

Precision measurements: Typical operating conditions were similar to those above except that pure nitrogen was leaked into the vacuum chamber to a desired pressure and ionized with an electron beam that gave 400 nA emission current. A 1.0 V trapping potential was sufficient to trap the ions. Because peak integral values were used for quantitation, it was necessary to ensure that each peak contained sufficient points to give reliable integral values using the algorithm supplied with the Nicolet computer. For this reason, 1000 time domain transients each with 64k data points were signal averaged. Calibration curves were constructed from the integrated peak area as a function of the ionization gauge pressure at approximately one hour intervals and one day intervals over pressures of 1.0×10^{-8} to 2.0×10^{-7} torr. All curves from one study were then graphed together for a qualitative assessment of the reproducibility. For a more quantitative measure of the precision, three independent measurements of the integrated peak area for nitrogen at a pressure of 5×10^{-8} torr were averaged for each time period. These average values were plotted as a function of time to show the reproducibility. The relative standard deviation (6) was then calculated for these values.

Resolution measurements: The chosen mass range (11 to 110 amu) determined the upper and lower excitation frequencies for the resolution measurements. The digitization frequency, and hence the detection bandwidth, was determined by the lower mass. Instrumental parameters were the same as in the precision measurements above, except that only 8k data points were taken at a pressure of 5×10^{-8} torr of perdeuterated benzene. This pressure provided enough ions for a reasonable signal but was low enough to minimize ion-molecule collisions which reduce resolution. An emission current of 900 nA was used. In addition to the permanent magnet, the electromagnet and the superconducting magnet were used to provide magnetic inductions of 0.2 to 1.0 and 3.0 T, respectively. In the case of the superconducting magnet, the mass range was limited to 18 to 110 amu because of the maximum digitization frequency available, so the measured resolution values were scaled for the lower mass using equation (2) to enable a comparison of resolution values for a wide range of magnetic inductions.

Signal-to-noise measurements: For signal-to-noise measurements, wideband spectra were acquired at 0.16 T for the permanent magnet, 0.2 to 0.5 T for the electromagnet and 3.0 T for the superconducting solenoid. All measurements were performed with 1.0 X 10^{-7} torr perdeuterated benzene, with instrumental parameters similar to those of the resolution measurements, except that 1.0 μA emission current was used and 500 time domain transients were signal averaged. For the permanent magnet S/N measurement, only 300 sweeps were signal averaged, so that measurement was scaled to 500 sweeps (7) by multiplying by $(500/300)^{1/2}$ to enable a direct comparison with the signal-to-noise values at different magnetic fields. Also, due to differences in the efficiency of collecting ionizing electrons for the analyzer cells used, an emission current of 500 nA was used in the superconducting system because the collection efficiency in that system is approximately one half the collection efficiency for the cell used with the electromagnet and permanent magnet. The S/N for a certain peak of interest was found by dividing the maximum signal intensity by an average baseline value, obtained from the mean of the response of 25 adjacent points from a region in the spectrum where no ions were present.

RESULTS AND DISCUSSION

Spectrum from the mass spectrometer utilizing a permanent magnet: Figure 1 shows a spectrum obtained with the permanent magnet system. The inverse dependence of resolution on mass for FTICR is apparent in the figure. Resolution values for helium (m/z 4) , water (m/z 18), nitrogen (m/z 28) and oxygen (m/z 32) are 729, 139, 93, and 67, respectively. Equation 2 predicts theoretical resolution values of 792, 176, 113, and 99 for these masses, which correspond to resolution values approximately 20% higher than those determined experimentally. This close agreement of theory and experiment with a magnet of low homogeneity supports the hypothesis that inexpensive low magnetic field permanent magnets can be used in FTICR mass spectrometry to provide useful information.

Precision: Figure 2 shows a series of calibration curves from the 4 hour reproducibility study. Five measurements of the integrated peak area for nitrogen as a function of ionization gauge pressure were taken at approximately one hour intervals and were used to construct calibration curves. As seen in the figure, qualitatively, no significant difference in the calibration curves, which represent the stability of the instrument over a period of 4 hours, can be seen. For a more quantitative measurement, three integrated peak areas for nitrogen at 5.0×10^{-8} torr from each hourly repetition were averaged and plotted as a function of time, as shown in figure 3. A relative standard deviation of 3.2% was obtained for this study. For a more long-term reproducibility study, similar measurements were taken daily over a period of 10 days. Figure 4 shows the calibration curves obtained. As seen in the figure, the curves look very similar to those obtained in the 4 hour precision study, with more variation in the integrated peak areas. Figure 5 shows the daily average of 3 measurements, as in figure 3, for nitrogen at a pressure of 5.0×10^{-8} torr as a function of time over the 10 day study. These measurements give a relative standard deviation of 11.7% for 11 independent measurements.

Resolution: Magnitude-mode resolution values for the molecular ion of perdeuterated benzene, m/z 84, scaled appropriately for a mass spectral scan of 8k data points from 11 to 110 amu as a function of magnetic field are given in Table I. The essentially constant resolution values over magnetic inductions of 0.16 to 3.0 T using the permanent magnet, the electromagnet, and the superconducting magnet indicate that the permanent magnet with low homogeneity can still provide adequate resolution values. The experimentally determined resolution values are about 20% lower than the theoretically predicted resolution value of 440 (equation 2) for this mass range and number of data points.

Signal-to-noise: Table I also gives S/N values for perdeuterated benzene for the permanent magnet, the electromagnet, and the superconducting magnet as a function of the magnetic induction. As predicted by equation 3, the S/N decreases with decreasing magnetic induction, although not as smoothly as one would hope.

The FTICR system based on a low induction permanent magnet with low homogeneity can give useful mass spectrometric information. Low magnetic field FTICR is particularly attractive to the modern analytical chemist because small, inexpensive permanent magnets can be used rather than bulkier more expensive electromagnets and superconducting magnets. Permanent magnets do not require a power supply nor do they require liquid helium temperatures to maintain their field. Lower stray fields are usually the case for small permanent magnets, particularly those permanent magnets with ion core yokes, such as the permanent magnet used in this study, which enable the placement of ionization gauges and pumps closer to the analyzer cell. This allows a more accurate measurement of the actual gas pressure in the analyzer cell and can reduce the pumping requirements of the system because higher conductances are possible. Lower magnetic fields produce lower cyclotron frequencies, hence the computer and electronics requirements are less critical than those for higher magnetic field FTICR operation. The geometry of currently available commercial systems hinders the placement of flanges for sample inlets, laser windows, and other apparatus close to the cell. The use of a small permanent magnet would allow a more flexible experimental setup.

Operation of FTICR mass spectrometers at low magnetic fields does provide several disadvantages. The most important is that, as shown earlier both theoretically and experimentally, S/N decreases with decreasing magnetic induction. Signal averaging can, in most cases, be used to increase S/N to an acceptable level. For a given digitizing frequency (and hence for a given digitizing time), the resolution decreases with decreasing magnetic fields. Longer acquisition times, available through the lower cyclotron frequencies in low magnetic field operation or increasing the number of data points, can usually be used to maintain adequate resolution, particularly for masses in the range of 12 to 100 amu. For FTICR at low magnetic fields, the selection of the ion excitation amplitude is much more critical than for higher magnetic field operation. This is because the radii of the cyclotron orbits are larger at lower magnetic fields. The margin between exciting an ion to a large enough orbit to provide a reasonable S/N and ejecting the ion from the cell by colliding it with the cell wall is much lower for low magnetic fields. Thus, "tuning" the instrument is more difficult because a much narrower range of excitation voltages will produce a reasonable mass spectrum. Superconducting magnets have vastly reduced the need for daily or even weekly mass calibrations in FTMS because of the stability of the magnetic field. On the other hand, the field of a permanent magnet which is not thermally insulated may drift over a period of hours, requiring a mass recalibration, particularly if extremely accurate mass determinations are required.

CONCLUSIONS

An FTICR mass spectrometer based on a permanent magnet provided a short-term precision that is acceptable for many analytical measurements. Similar resolution values obtained with a permanent magnet system and a superconducting magnet system for a given mass range indicated that spectra of adequate resolution can be obtained at low magnetic fields. The S/N is much lower for low magnetic fields, so to achieve a given S/N a tradeoff between spending longer times for signal averaging with a less expensive instrument and shorter acquisition times possible with more expensive high magnetic field systems exists.

CREDIT

This material is based upon work supported under a National Science Foundation Graduate Fellowship and by the Office of Naval Research. A portion of this paper was presented at the 34th Annual Conference on Mass Spectrometry and Allied Topics, June 8-13, 1986, Cincinnati, Ohio.

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TABLES

Table I: Resolution and S/N for m/z 84 as a Function of Magnetic Induction for a Mass range of 11 to 110 amu

Magnetic Induction (T)	Resolution	S/N
3.0 (superconducting)	358	2250
1.0 (electromagnet)	333	477
0.5 (electromagnet)	346	332
0.3 (electromagnet)	389	302
0.2 (electromagnet)	355	125
0.16 (permanent magnet)	406	75

FIGURE CAPTIONS

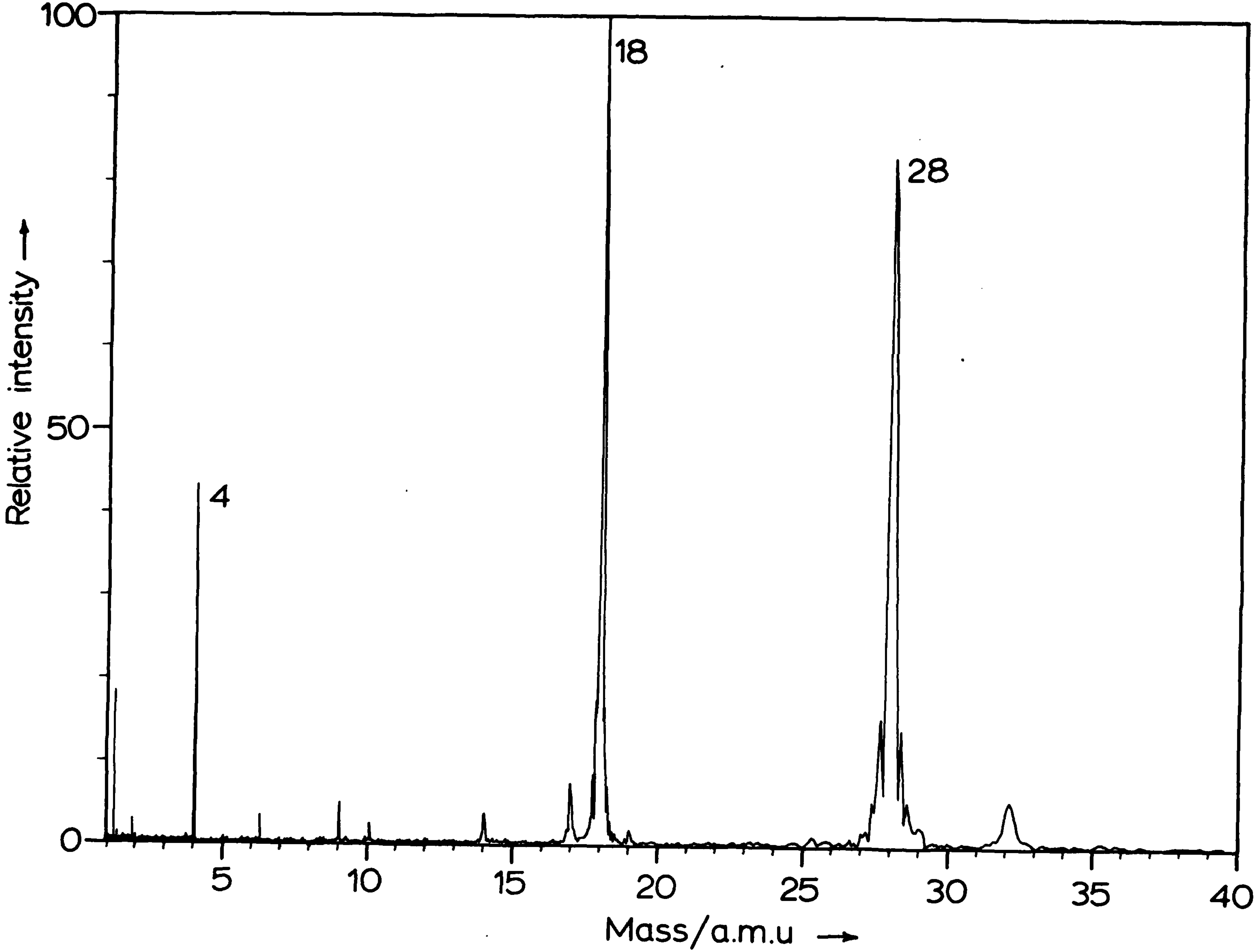
Figure 1: Permanent Magnet (0.16T) FTICR Spectrum of Helium, Water, and Air.

Figure 2: Short-Term Reproducibility of Calibration Curves for N_2 (m/z 28).

Figure 3: Short-Term Precision measurements: the average of three independent integrated peak area measurements are plotted as a function of time.

Figure 4: Long-Term Reproducibility of Calibration Curves for N_2 (m/z 28).

Figure 5: Long-Term Precision measurements: the average of three independent integrated peak area measurements are plotted as a function of time.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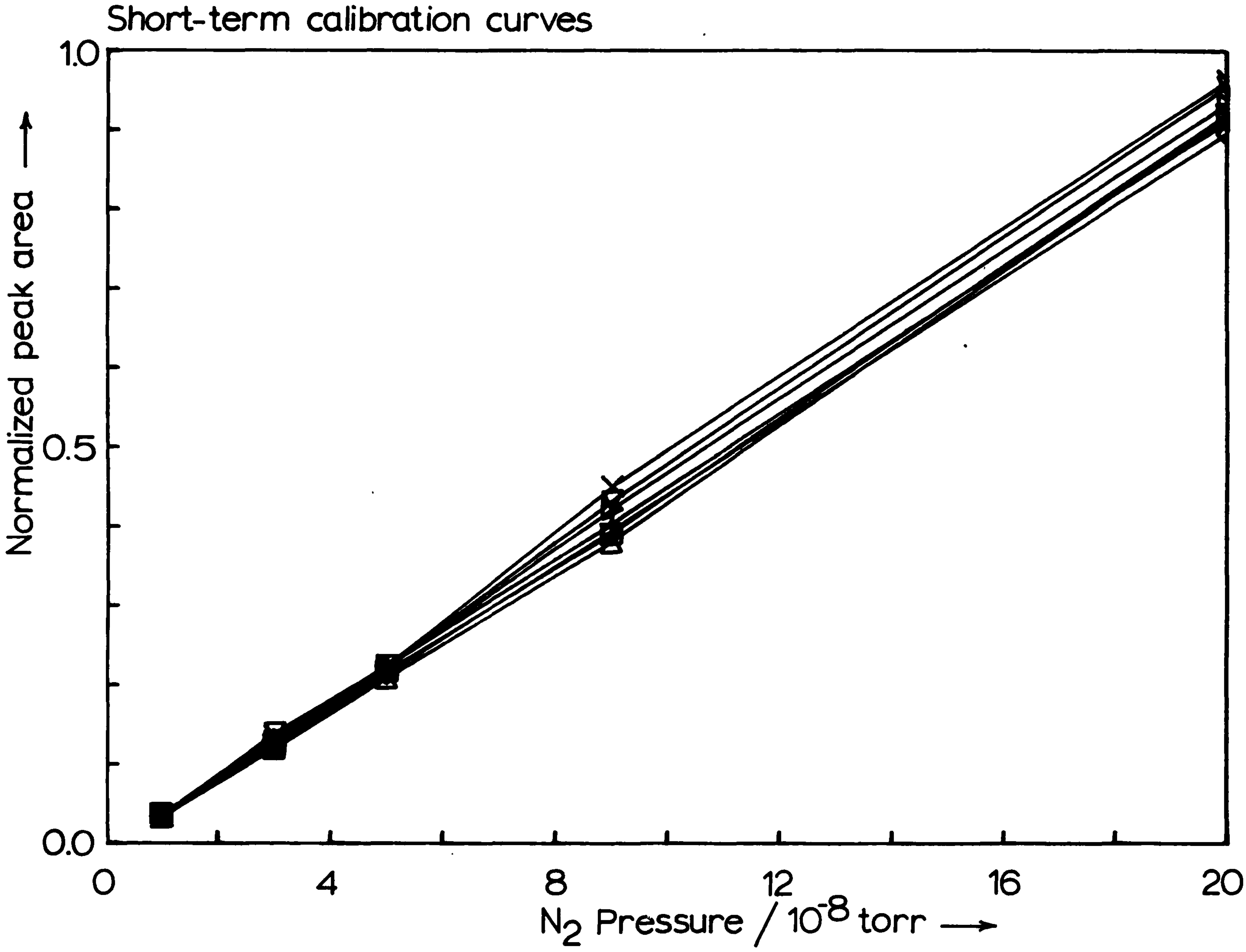
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16
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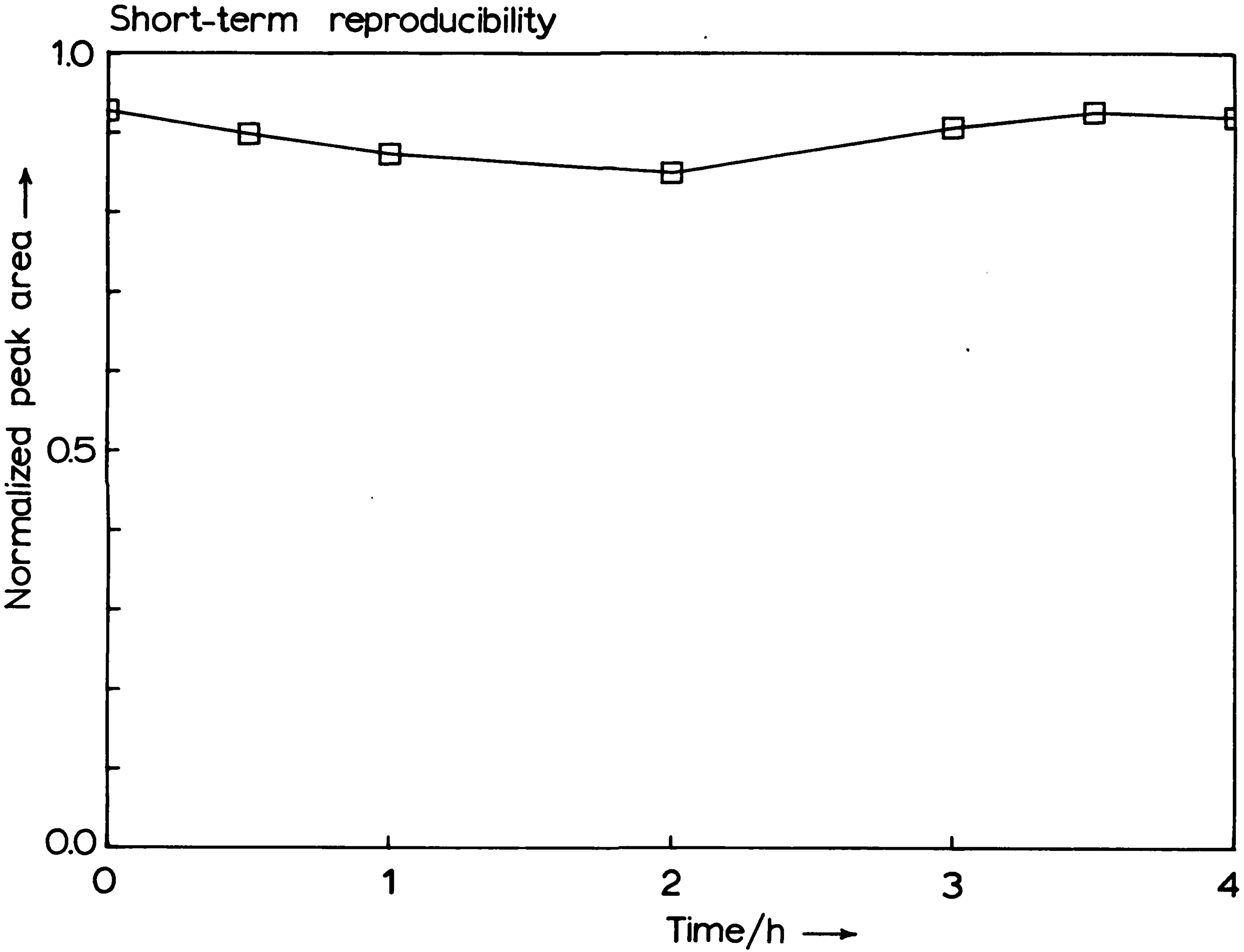
N$_2$ Pressure / 10^{-8} torr →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3
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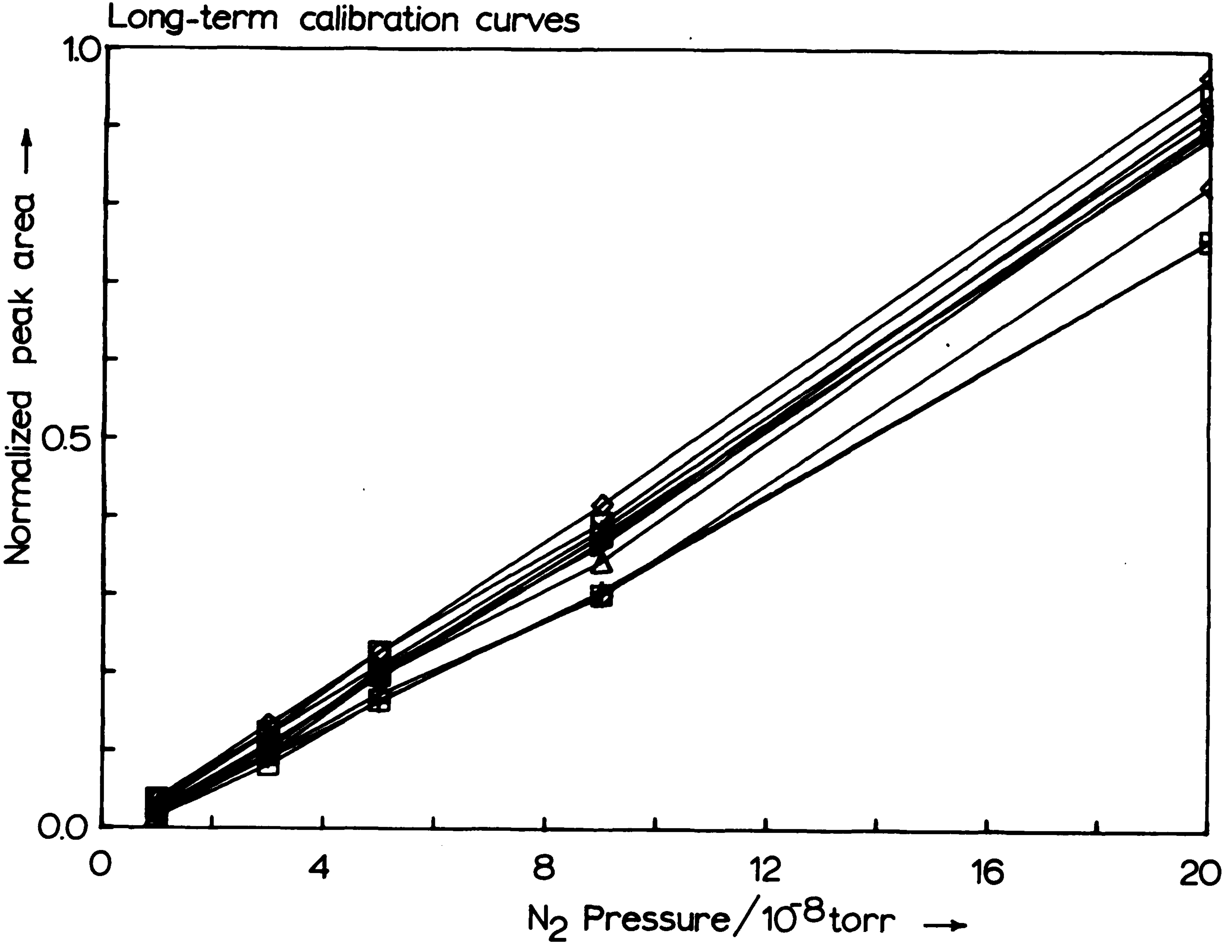
Time/h ⟶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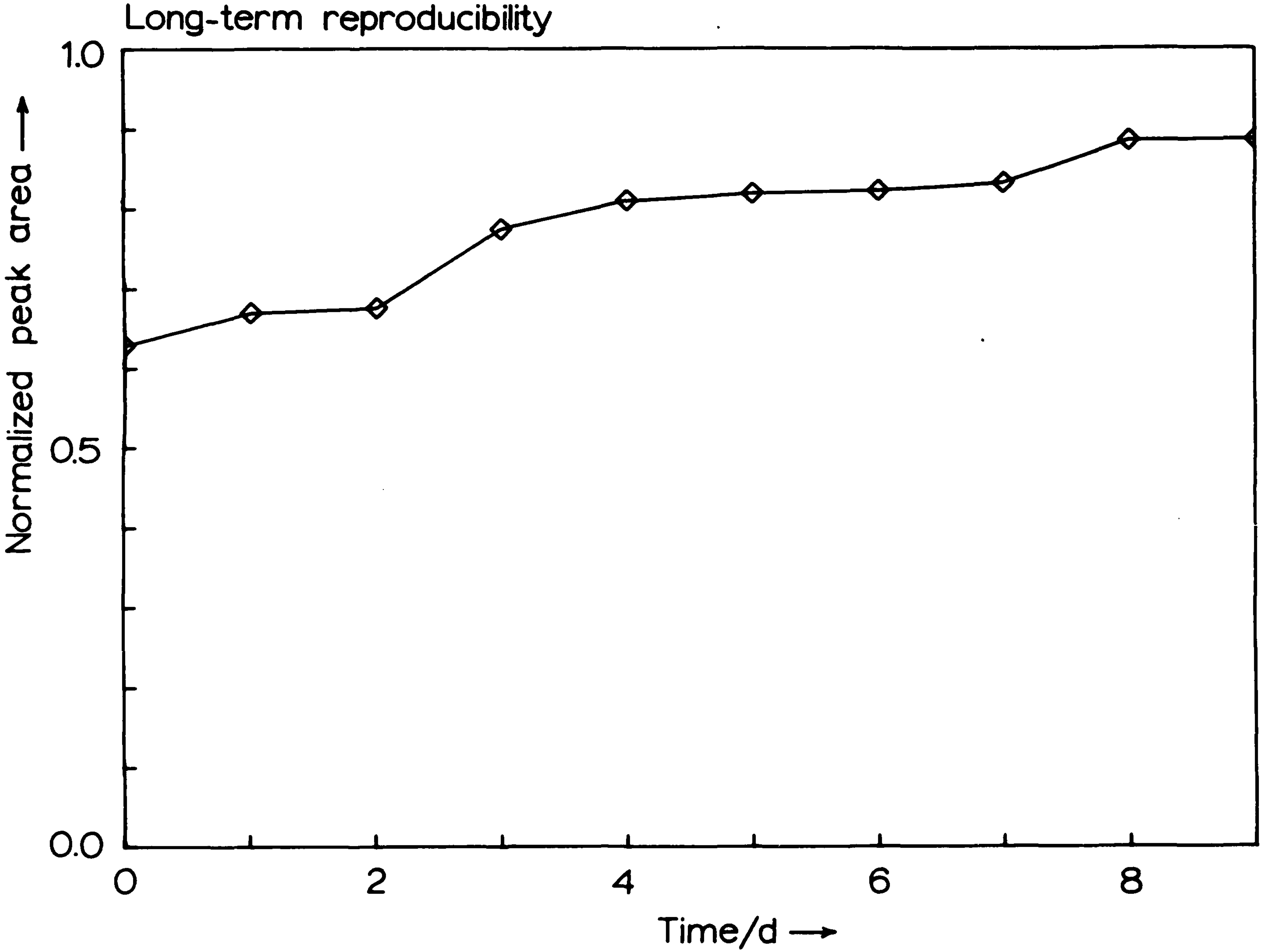
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