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Improved Stable Nitrogen Isotope Ratio Measurements of Natural Gases

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A system has been developed at BGR for rapid and precise nitrogen isotopic ratio measurements on natural gases in northern Germany using a gas chromatograph coupled with an isotope ratio mass spectrometer (GC/IRMS). The main advantage of the GC/IRMS system relative to conventional techniques is the analysis of gases with varying nitrogen concentrations down to 0.1% in routine operation. Small sample size down to 10 nmol of nitrogen is sufficient for precise measurement within the 1σ range of ± 0.3 to $\pm 0.5\%$. Care was taken to avoid sample contamination by atmospheric nitrogen during measurement, which in other preparation systems occasionally yields systematic errors of up to several per mill. The system was designed for user friendly, fast operation with computer-aided data acquisition and calculations. A comparison of reanalyzed with already published $\delta^{15}\text{N}$ values for nitrogen gas from several natural gas fields in northwest and southern Germany reveals significant differences which depend on the nitrogen concentration. A careful handling of the data is recommended.

BGR is conducting a research project titled "Deep Gas" to evaluate the hydrocarbon potential of pre-Westphalian sediments in northern Germany. Within this project, the molecular and isotopic composition of gases from more than 200 natural gas wells have been analyzed to detect any components from pre-Westphalian sources in the gases from the main source rock, Upper Carboniferous coal seams. Apart from other gaseous components (e.g., hydrocarbon gases, carbon dioxide, hydrogen sulfide, and noble gases), the concentration and the isotopic composition of molecular nitrogen is used to obtain information on the source(s) of these natural gases.

The concentrations and isotopic compositions of nitrogen from various gas fields in the Northwest German basin and the Molasse area of southern Germany have already been presented.^{1–5} Similar data are available from oil and gas fields in East Germany.⁶ Several of these natural gas wells are still producing and could be resampled and analyzed during the Deep Gas project. Nitrogen concentrations were found to be in good agreement with published data. But significant

differences between the isotope ratios of nitrogen were found while conventional preparation techniques were being used, particularly in resampled gases from West Germany. Consequently, great effort was made to avoid analytical errors in the current project by installing and testing different preparation techniques.

Stable isotope ratios are usually measured using a double-inlet double-collector mass spectrometer, which allows alternate measurement of ion currents generated from the sample and the reference gas. For nitrogen isotope determination, the ion currents for mass 29 ($^{15}\text{N}^{14}\text{N}^+$) and mass 28 ($^{14}\text{N}^{14}\text{N}^+$) are detected simultaneously for a fixed integration time, giving a signal ratio $R_{\text{sa}} = ^{15}\text{N}_{\text{sa}}/^{14}\text{N}_{\text{sa}}$, which is to be compared with the signal ratio R_{st} of the laboratory reference gas. Isotope values are expressed in the common δ -notation:

$$\delta^{15}\text{N}_{\text{sa}} = ((R_{\text{sa}}/R_{\text{st}}) - 1) \times 1000 \quad (1)$$

To allow comparison internationally, the data were recalculated as follows to $\delta^{15}\text{N}_{\text{int}}$:

$$\delta^{15}\text{N}_{\text{int}} = \delta^{15}\text{N}_{\text{sa}} + \delta^{15}\text{N}_{\text{ref}} + (\delta^{15}\text{N}_{\text{sa}}\delta^{15}\text{N}_{\text{ref}}) \times 10^{-3} \quad (2)$$

where $\delta^{15}\text{N}_{\text{ref}}$ is the value for the laboratory reference gas referred to the international standard gas.⁷ Since nitrogen in air is considered to be the largest, isotopically homogeneous nitrogen reservoir on earth, it is used as international standard with a mean $\delta^{15}\text{N}$ value of $0.0 \pm 0.25\%$.⁸ To illustrate the natural variation in this value, the ranges of $\delta^{15}\text{N}$ values for various natural substances are shown in Figure 1.⁹ As can be seen, the total range extends from $\delta^{15}\text{N} = -40\%$ to $+100\%$, but is restricted for earthborne substances from -20% to $+20\%$. The accuracy of isotope measurements of gaseous nitrogen is given in the literature as ± 0.3 to $\pm 0.5\%$,⁸ mostly due to the trivial problem of air contamination:

(a) Small amounts of air contaminating the sample will shift the $\delta^{15}\text{N}$ value of the sample toward that of air nitrogen.

(b) Fluctuating amounts of oxygen in the ion source due to contamination with air produce fluctuating ion currents by changing its properties.

(c) Mass interference due to the formation of NO_x and CO_x from nitrogen and carbon ions represents a further problem for nitrogen isotope analysis. Carbon monoxide,

(1) Eichmann, R.; Plate, A.; Behrens, W.; Kroepelin, H. *Erdöl, Kohle, Erdgas, Petrochem.* 1971, 24 (1), 2–7.

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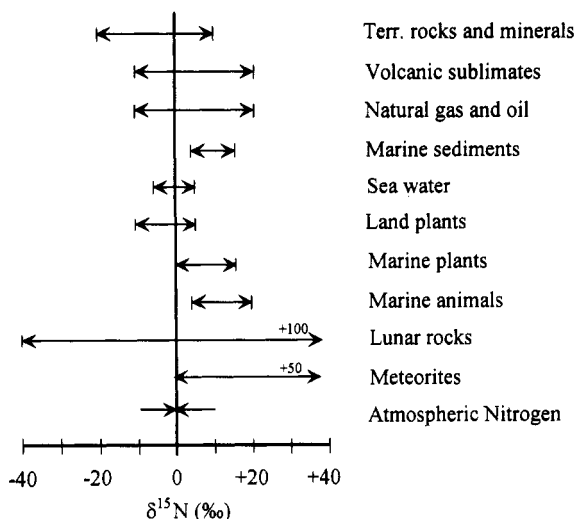


Figure 1. Distribution of nitrogen isotope data for natural substances (after Kaplan⁹).

$^{13}\text{C}^{16}\text{O}^+$, generated in the ion source by electron cracking of hydrocarbons and oxygen or via carbon dioxide (or directly), especially masks the $^{15}\text{N}^{14}\text{N}^+$ signal at mass 29 due to the higher natural abundance of ^{13}C (1.1%) compared to ^{15}N (0.36%).¹⁰

All three processes will significantly alter the measured sample isotope ratio (R_{sa}) and $\delta^{15}\text{N}$ value. To avoid this, sample and standard gases must be prepared very carefully (with respect to prevention of entry of atmospheric nitrogen and oxygen) and must be checked by use of reference gases with isotope ratios different from that of air. Taking this into account, different approaches were used in our laboratory for the separation and analysis of nitrogen from natural gas.

PROBLEMS IN CONVENTIONAL PREPARATION TECHNIQUES

The first method developed used a closed-system combustion line (a modified version of that of Behrens et al.¹¹) shown in Figure 2. The hydrocarbons of the natural gas are converted to CO_2 and H_2O by use of a CuO oven (reaction temperature 900°C). Any oxygen present is removed in a Cu oven (reaction temperature 900°C). The combustion products are trapped in the cold trap at liquid nitrogen temperature ($\text{N}_2(\text{l})$). The natural gas is circulated in the system with a Toepler pump to achieve complete combustion of the hydrocarbons. Non-condensable components, i.e., nitrogen and the rare gases, are transferred to a dual-inlet mass spectrometer (MAT 250). Sample sizes of 5–20 mL of natural gas (which corresponds to N_2 quantities of 50–200 μmol) are required to obtain sufficiently strong mass spectrometer ion signals so that the resulting $\delta^{15}\text{N}$ values will be within the 1σ error limit of $\pm 0.5\%$.

The major disadvantage of this system is the time-consuming preparation: the amount of time depends on the nitrogen concentration of the sample. Complete combustion of samples with nitrogen concentrations below 10% require preparation times of up to 1 h to approach the actual isotope

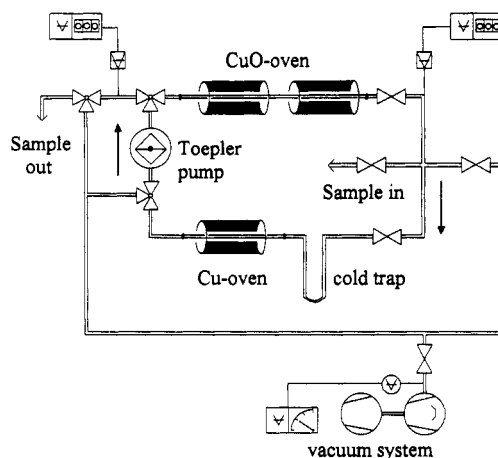


Figure 2. Combustion system for nitrogen preparation: The sample is circulated through the system by a Toepler pump. The CuO oven is used for oxidation of the hydrocarbons, and the Cu oven for removal of O_2 . The combustion products (CO_2 and H_2O) are removed by the liquid nitrogen cold trap.

value. If the preparation time is too short, i.e., incomplete combustion of hydrocarbons, the measured isotope ratio deviates from the actual one due to mass interference by unremoved hydrocarbons. When samples with very low nitrogen concentration (below 2%) are prepared, the real $\delta^{15}\text{N}$ value is never obtained owing to contamination with air nitrogen through small leaks in the system. Thus, this system can be used only for the preparation of samples containing more than 10% nitrogen. Below this limit, the error in the measured isotope data will be greater than 1%, increasing with decreasing nitrogen content.

A second method consists of the separation of nitrogen and hydrocarbons using a GC¹² combined with the trapping of the eluted nitrogen with a molecular sieve at $\text{N}_2(\text{l})$ temperature. The GC, operated isothermally at 50°C , is equipped with a packed column (adsorbent 5-Å molecular sieve) and a helium head pressure of 180 kPa. Sample sizes of up to 5 mL of natural gas are used, depending on the nitrogen content (10–70%). The length of time required to trap the eluted nitrogen peak varies between 20 and 40 s, also depending on the nitrogen content.

The disadvantage of this method is the differential adsorption of the $^{15}\text{N}^{14}\text{N}$ and $^{14}\text{N}^{14}\text{N}$ molecules on the cooled molecular sieve. We have found that only sophisticated heating and cooling cycles (between 150°C and room temperature for 10 min) will release nitrogen without any isotope fractionation, which is confirmed by the experience of others.¹³ In addition, column bleeding (of CO_2) will increase the nitrogen background level during the trapping of the nitrogen. Warming up of a cooled molecular sieve from $\text{N}_2(\text{l})$ to ambient temperature without cycling the temperature from warm to cold several times will release nitrogen depleted in $^{14}\text{N}^{14}\text{N}$. This indicates a weaker molecular interaction between the adsorbent and the $^{15}\text{N}^{14}\text{N}$ molecule than with the $^{14}\text{N}^{14}\text{N}$ molecule. Isotopic equilibration is reached after 50 min with a close approach to the actual isotope value. If this desorption

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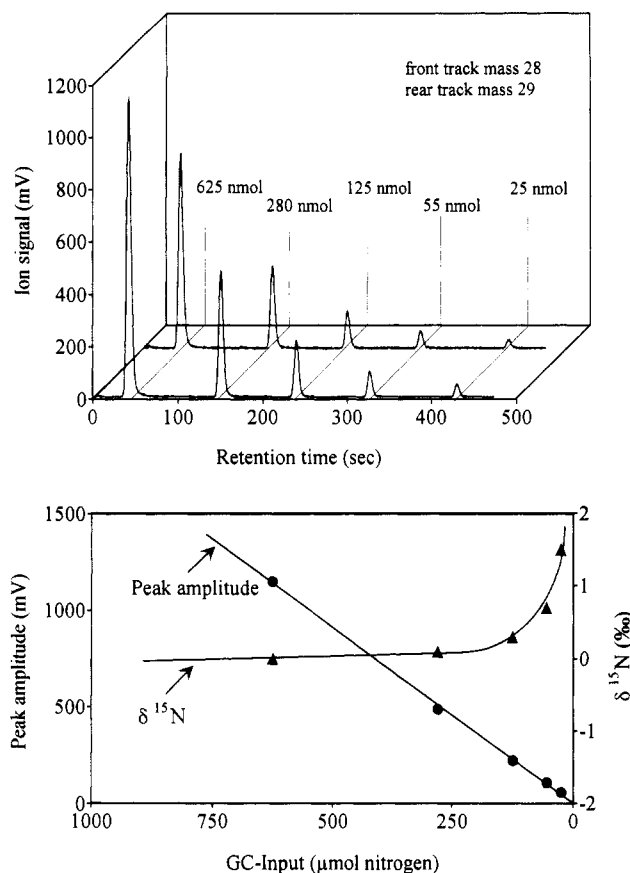


Figure 3. (Top) Five replicate analyses of the standard gas LabSt1 with decreasing quantities of nitrogen input to the GC (marked in nmol of N_2). (Bottom) Calculated peak amplitudes from top panel. The straight line illustrates the linear correlation between nitrogen peak amplitude and sample size. The curved line shows the trend of $\delta^{15}N$ values as a function of sample size (the $\delta^{15}N$ value of the first sample was set to 0.0‰ for calibration).

behavior is ignored, isotope fractionation can reach several per mill and is particularly prominent for samples enriched in ^{15}N .

EXPERIMENTAL GC/IRMS SETUP

To overcome all the above-mentioned problems, we connected a gas chromatograph directly to an isotope ratio mass spectrometer (GC/IRMS). This technique, well established since the late 1970s, allows high-precision measurement of isotope ratios, even with small sample sizes.^{14,15} To demonstrate the advantage of this technique, one of our records of an air standard is shown in the upper part of Figure 3. Calculated $\delta^{15}N$ values from the GC/IRMS data (lower part of Figure 3) agree within 1‰ for sample sizes down to 50 nmol of N_2 , which is equivalent to 5-nmol N_2 input into the ion source (see System Calibration).

The GC component of the system, depicted in Figure 4 (Packard 430), has a column length of 3 m and a diameter of $1/8$ in. and is packed with 5-Å molecular sieve as adsorbent. The GC is set to a constant temperature of 75 °C with a head pressure of the He carrier gas of about 270 kPa. The inlet system to the GC has four inlet ports (valves M1–M4), which

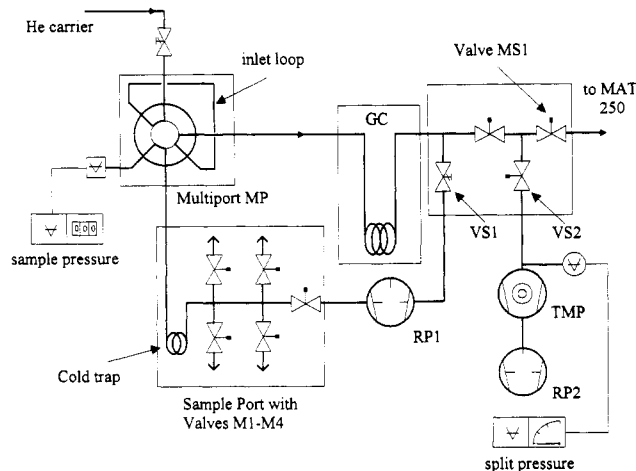


Figure 4. GC/IRMS system for measuring the nitrogen isotope ratio. For details, see text.

can be separately switched to the multiport valve (valve MP) and contains a 200- μ L inlet loop. A cold trap containing no adsorbant connects these two components. Three inlet ports are permanently connected to plastic bags (Linde Plastigas) filled with different standard gases. The fourth inlet port is used for input of the sample, typically in 100–500-mL glass bottles. The GC inlet system as a whole can be evacuated to a pressure of 1 Pa using a rotary pump (RP1). A semiconductor pressure gauge is used to measure the pressure in the inlet system. Inlet pressures of 50 Pa to 50 kPa are possible, corresponding to sample quantities of 5–5000-nmol nitrogen GC input, respectively.

The GC output is connected directly to the MS (Finnigan MAT 250; no differential pumping) through valve MS1. This valve allows purging of interfering gases, e.g., methane and carbon monoxide. The GC column pressure is reduced prior to entry of the sample into the MS (typical MS working pressure 5×10^{-4} Pa). This is done using simple T-pieces, the first connected to a rotary pump (RP1) via needle valve VS1 and a second connected to a turbo molecular pump (TMP) via valve VS2. The common split ratio can be adjusted (using valve VS1) according to the nitrogen concentration of the sample and is normally set to a ratio of 1:10. Thus, an input of 5–5000 nmol of nitrogen into the GC results in an input of 0.5–500 nmol of nitrogen to the MS ion source.

GC parameters (temperature and head pressure) and column material are chosen to achieve good peak separation, as can be seen in Figure 5, which shows the ion signal records of a standard sample at mass 29 (front track) and at mass 28 (rear track). The sample (1% O_2 , 2% N_2 , 95% CH_4 , 1% CO , 1% CO_2) was introduced at an inlet pressure of 35 kPa. The O_2 , N_2 , CH_4 , and CO peaks are marked in Figure 5 together with their quantities and retention times (75, 90, 120, and 210 s, respectively). As can be seen, all input components give a peak at mass 29 except CO_2 (which is trapped on molecular sieve of the GC). After the system has been operated for 1 week, the column must be reactivated by heating for several hours at 350 °C to prevent overloading the column with CO_2 , which would result in continuous bleeding of CO_2 from the column, resulting in mass interference in the MS.

The appearance of the oxygen signal at mass 29 can be explained by any of several mechanisms (see introduction).

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(15) Brand, W.; Tegtmeier, A.; Hilkert, A. *Org. Geochem.*, in press.

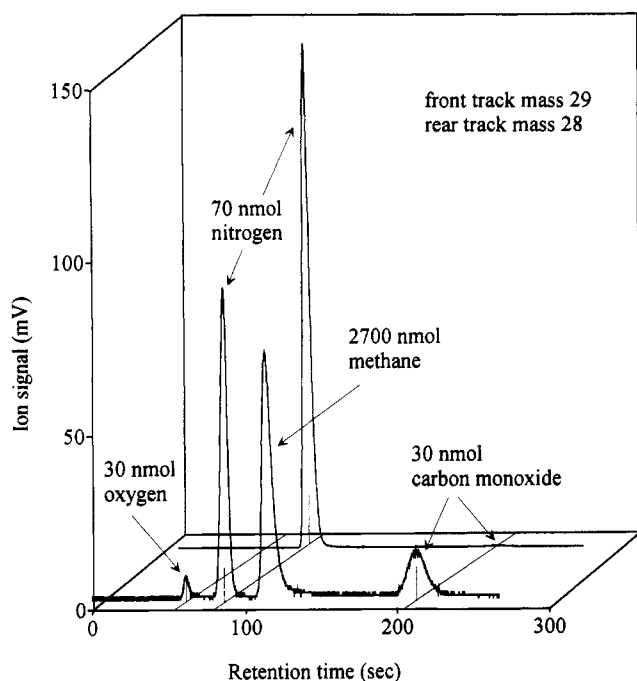


Figure 5. GC/IRMS separation of a test gas (1% O₂, 2% N₂, 95% CH₄, 1% CO, 1% CO₂). The relevant gas quantities are indicated. Both tracks verify the component separation of our GC/IRMS system.

The methane peak can be explained by partial conversion into ¹³CO, which gives a strong peak at mass 29. Carbon monoxide itself in the gas sample also causes a peak. In contrast, the track at mass 28 shows a large nitrogen peak but only a small CO "hump", with no detectable oxygen or methane. When the ratios (¹⁵N/¹⁴N) of the signals of the two mass tracks are calculated for each of the peaks at mass 29, oxygen, methane, and carbon monoxide give larger signal ratios than nitrogen (cf. Figure 8). Hence, without good peak separation of O₂, N₂, and CH₄, as shown in Figure 5, the ratio of the nitrogen signal may be altered significantly by the contribution of oxygen and/or methane to the nitrogen peak.

The cold trap (at N₂(l) temperature) between the inlet port and the inlet loop is used to remove condensable components, such as higher hydrocarbons, carbon dioxide, and water, and prevents overloading of the column with CO₂, as mentioned above. Thus, reactivation of the column is not necessary. To illustrate the influence of the cold trap, Figure 6 shows ion signal records of a standard sample measurement (1.75% nitrogen, 25 nmol of nitrogen) with and without the cold trap. When the two tracks are compared, it is seen that the nitrogen peak is larger by a factor of 5 when the cold trap is used and the methane peak is reduced by a factor of 95 (i.e., not all of the methane is removed by the cold trap). Leakage from the inlet system must be (and is) very low since the cold trap functions as a cryopump and even small leaks will increase the nitrogen background. Measurements of blanks show nitrogen leak peaks with a maximum amplitude of 5 mV (this corresponds roughly to a sample size of 500 pmol of nitrogen), which is negligible compared to a typical sample peak with a magnitude of 225 mV as shown in Figure 6.

SYSTEM CONTROL AND DATA PROCESSING

The mass spectrometer is connected to a PC by an IEEE interface. A QuickBasic program controls the MS and handles

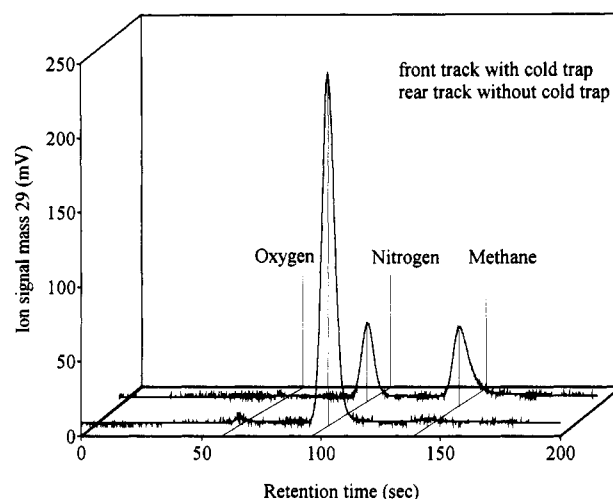


Figure 6. Ion signal record for LabSt1 (98.25% CH₄) at mass 29 with and without cold trap. With removal of most of the methane, the nitrogen peak is enlarged.

data acquisition and analysis. The ion signals at the two collectors at masses 28 and 29 are simultaneously recorded with an integration time of 100 ms. Several GC/IRMS analyses are necessary for each sample. For each analysis, the sample is introduced (using one of the four inlet ports) through the cold trap into the evacuated inlet loop and then flushed onto the GC column. After an idle time of 60 s (in which no data are recorded in order to minimize record lengths), the transfer line is opened to the MS (valve MS1; see Figure 4). The oxygen and nitrogen peaks are recorded, methane and carbon monoxide are purged (with valve MS1 closed), and the program returns to idle mode. On-line monitoring of the oxygen peak allows detection of contamination of the sample with air, and this peak is later used to calculate the air-free nitrogen isotope ratio.

Five analyses are made for each sample (Figure 7). First, an air standard (LabSt1; see Table 1) is measured to determine the zero point of the $\delta^{15}\text{N}$ scale, followed by two standard gases (LabSt2, for which a $\delta^{15}\text{N}$ value of +13.9‰ was obtained, and LabSt4 with $\delta^{15}\text{N} = -2.6\text{‰}$), for cross referencing, and finally the sample is measured twice. The beginning and end of peak integration are marked in enlargements of the curves for LabSt1 and the first sample, as well as the approximate baseline (for calculation, see below). Comparison of the ratio of the nitrogen peak maximum (P^{N}) to the oxygen peak maximum (P^{O}) in the two enlarged sections ($P^{\text{N}}/P^{\text{O}} = 200$ for diluted air LabSt1) indicates that the small amount of air contamination of the sample ($P^{\text{N}}/P^{\text{O}} = 1750$) can be neglected. Whenever this signal ratio becomes comparable to that of LabSt1, it is used to calculate the amount of contaminating air nitrogen admitted to the sample during sampling. It was determined that $P^{\text{N}}/P^{\text{O}}$ is linear for LabSt1 for GC inputs down to 50 nmol of nitrogen.

After each measurement, the data are stored and processed as follows: Since the minimum MS signal resolution is ± 1 mV (MAT 250, constructed in 1980), it is impossible to determine the peak baseline with a higher precision than 1 mV. Taking this into account, the error in the determination of the peak area (and consequently that of the isotope ratios) depends on the ratio of peak height to baseline noise and can reach $\pm 5\text{‰}$ if the peak has an amplitude of less than 50 mV.

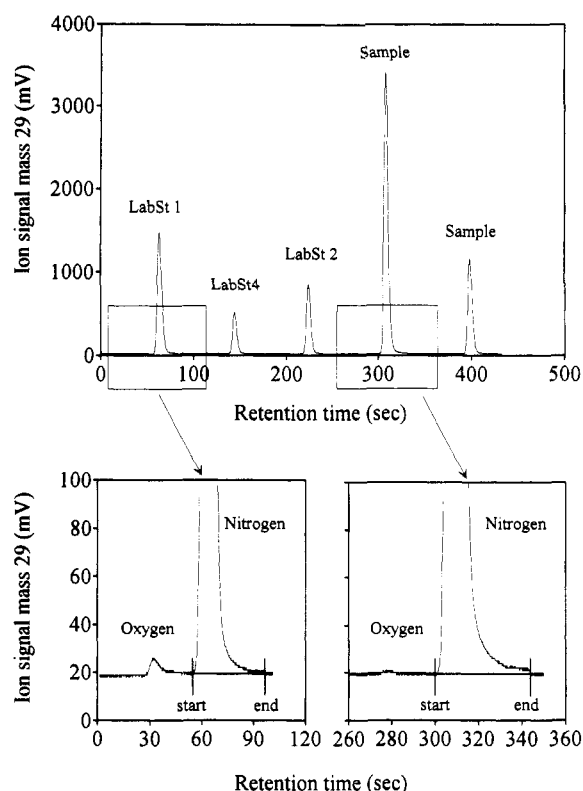


Figure 7. Complete GC/IRMS measurement cycle, with three standards and two replicate sample analyses. Integration tick marks and calculated baseline are shown for LabSt1 and a sample.

Table 1. Nitrogen Concentrations and $\delta^{15}\text{N}$ Values of International and Laboratory Standards Used for GC/IRMS Measurements

	N_2 (%)	$\delta^{15}\text{N}$ (‰)		runs
		ref 14	this work	
NGS-1	14.2	16.2	16.0 ± 0.2	10
NGS-1	3.6	16.2	15.9 ± 0.4	3
NGS-1	1.8	16.2	15.7 ± 0.4	3
NGS-2	13.9	5.0	5.5 ± 0.3	5
air	78.8	0.0	-0.1 ± 0.1	10
LabSt1	1.8		0.0 ± 0.4	100
LabSt2	5.0		13.9 ± 0.3	100
LabSt3	6.0		-6.7 ± 0.3	100
LabSt4	1.3		-2.6 ± 0.5	100

To overcome this, the program starts smoothing the data for both mass tracks to reduce the signal noise by calculating the (weighted) mean value of each data point with respect to surrounding data points. Taking into account adjacent data points in forward and backward directions, short-time fluctuations (like system noise) are smoothed out while long-time fluctuations (true GC peaks) are preserved. To illustrate the advantage of the smoothing technique, a plot of the signal ratio (R , ion signal mass 29/28) before and after (bold line) smoothing is shown in the lower part of Figure 8 for the oxygen, nitrogen, and methane peaks (LabSt1 from Figure 7). It can be seen that the shape of the nitrogen ratio peak fluctuates around the ratio of air nitrogen. This is due to the time offset between peak signals at mass 28, which leaves the GC before mass 29, owing to the properties of the column adsorbent. Smoothing reduces the background fluctuations by a factor of 10 with no significant deviation between the raw and smoothed data with respect to peak amplitude and shape of the nitrogen ratio peak (upper part of Figure 8).

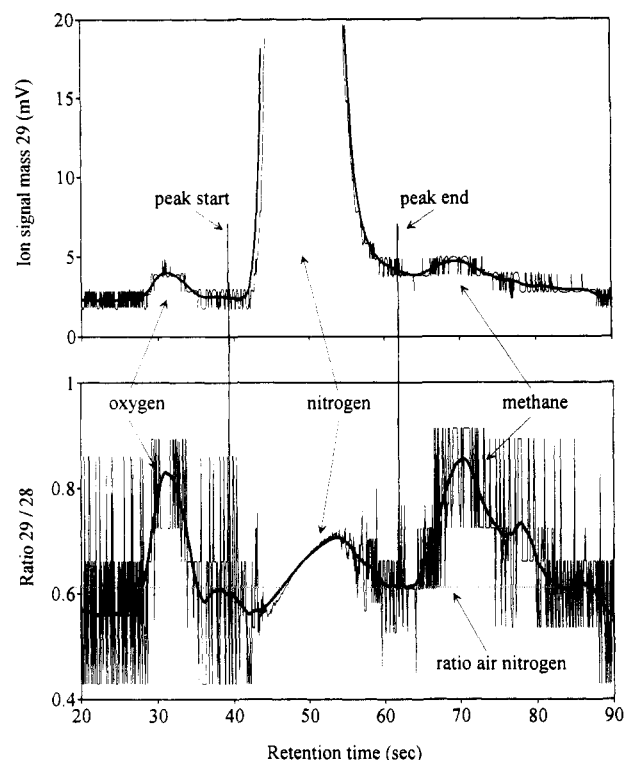


Figure 8. Raw and smoothed (bold lines) ion signal data for mass 29 (upper plot) and signal ratios (lower plot). Peaks for oxygen, nitrogen, and methane, as well as the integration tick marks for the nitrogen peak, are marked.

After the data have been smoothed, a search for peaks with a minimum peak amplitude is started (only for mass 28). The beginning and end of each peak are determined when the slope between adjacent data points exceeds a selected value. Identical peak start and end times are used for both mass tracks, since the time offset between the peak signals at masses 28 and 29 is less than the response time of the system (100 ms). For each peak, the baseline is then calculated by a least-squares fit (using a linear or a parabolic function) based on 100 data points before and after the peak. Peak areas are calculated by Simpson integration of intensity data after subtraction of the corresponding baseline counts. The mass 29/28 signal ratios are then determined for each peak, which are then normalized to the isotope ratio of standard air (LabSt1 with $\delta^{15}\text{N}$ set to 0.0‰). This calibration is checked by using two other well-known standards, as described above.

SYSTEM CALIBRATION

The isotope scale is calibrated using three international reference gases: air nitrogen, NGS-1, and NGS-2.¹⁶ The values obtained for these standards are used to calibrate our laboratory standards (cf. Table 1), which were prepared from well-known pure nitrogen standards (LabSt2–4) and from air (LabSt1, including air oxygen) by dilution with methane. The nitrogen concentrations of our LabSt's are chosen to match the N_2 concentration of most natural gases in Germany. For replicate measurements, our isotope values are within $\pm 0.5\text{‰}$

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Table 2. Comparison of Published Isotope Data¹⁻⁵ from Several German Natural Gas Fields with Those Measured in the BGR Laboratory

gas sample	N ₂ (vol %)	δ ¹⁵ N (‰)				
		this work	refs 3 and 4	ref 2	ref 1	ref 5
NW Germany						
Adorf Z5	4.9	+3.1		-6.3		
Annaveen Z4	36.7	-1.1	-8.4			
Barrien 2T	18.7	+9.2			+3.4	
Barrien 5T	18.1	+10.2			+3.4	
Bentheim 10	6.2	-2.8			-7.9	
Emlichheim Z6	4.0	-2.2	-8.8			
Fehndorf 3Z	19.1	-1.5	-7.6			
Frenswegen 5	4.5	-3.1	-9.8	-9.4		
Getelo Z1	1.8	+6.7	-14.6			
Greetsiel Z1	3.5	+12.6	+1.3			
Groothusen Z5	8.8	+15.4	+7.7			
Groothusen Z6	8.4	+15.3			+6.4	
Itterbeck-Halle Z8	1.0	+16.4		-10.8		
Itterbeck-Halle Z10	1.0	+17.0	-13.7			
Kalle Z4	2.3	+2.3	-9.7	-8.8		
Norddeutschland 5	5.0	-2.3			-8	
Norddeutschland 8	5.0	-2.4			-8	
Ratzel Z4	2.2	+11.1	-8.7			
Rehden 24	6.7	-1.1	-6.6		-6.6	
Rehden 5	7.0	-2.1			-6.3	
Rehden 9	7.0	-1.5			-6.6	
Rehden T1	6.3	+1.3			-6.6	
Uelsen T2	14.4	+1.1		-5.5		
Uttum Z1	2.7	+12.8	+1.1			
Wielen Z4	2.0	+11.4	-11.8	-7.5		
Wustrow West Z1	57.1	+7.9	+4.1			
South Germany						
Fronhofen 3	2.7	+3.7				-5.3
Hohen Linden 2	0.4	-5.2				-10.5
Itzenham-West 1	0.9	+2.0				-6.9
Itzenham-West 3	1.0	+3.7				-6.8
Kirchdorf 3	2.0	+3.9				-3.6
Moosach 1	0.4	-5.6				-11.9
Schmidthausen	1.9	+2.5				-6.5

(1 σ) of the literature values for the international standards¹⁶ (Table 1). The NGS-1 standard (14.2% N₂) was diluted with methane to nitrogen concentrations of 3.6% and 1.8% to obtain a concentration closer to those of our samples. The small difference between the $\delta^{15}\text{N}$ values for the three concentrations is within the limit of our precision (see Table 1), but may also be due to a small amount of nitrogen in the methane used for dilution.

The linearity of the GC/IRMS system was checked using LabSt1. The upper part of Figure 3 shows five replicate analyses of the standard gas with decreasing quantities of nitrogen input to the GC. The corresponding $\delta^{15}\text{N}$ values and peak amplitudes are shown in the lower part of Figure 3 as a function of nitrogen sample size. The correlation coefficient for peak amplitude and sample size is $r = 0.99$. Hence, the peak amplitude (together with the known inlet pressure) can be used to determine the nitrogen content of unknown samples.

The calculated $\delta^{15}\text{N}$ values agree within the 1 σ range of $\pm 0.5\text{‰}$ for samples with as little as 50 nmol of nitrogen. With a split ratio of 1:10, this is equivalent to an input of 5 nmol of nitrogen into the MS, where the signal-to-noise ratio reaches a value of $S/N = 10$. Only the smallest peak (peak maximum of <100 mV and $S/N < 10$) falls out of line. To extend measurements to nitrogen quantities lower than 50-nmol GC

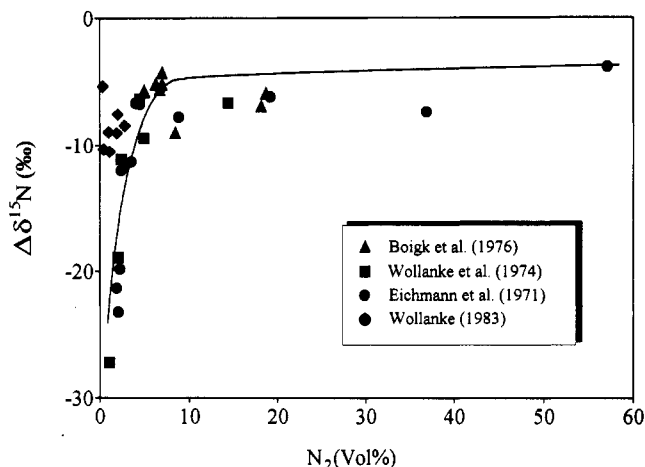


Figure 9. Differences between published $\delta^{15}\text{N}$ values¹⁻⁵ for several natural gas fields in northern and southern Germany and those measured in the BGR laboratory. The approximate regression line depicts the relationship between $\Delta\delta^{15}\text{N}$ and N₂ content.

input, the split ratio (valve VS1 in Figure 4) can be adjusted to increase the S/N ratio above this limit.

CONCLUSIONS

A new and reliable method has been applied to a MAT 250 mass spectrometer for the analysis of stable nitrogen isotope ratios. The GC/IRMS system is designed to satisfy the requirements of a low leak rate to avoid air contamination, an adjustable GC inlet system, sufficient GC separation of oxygen, nitrogen, and hydrocarbons to minimize mass interference, and last, but not least, fast and easy handling. International standards guarantee $\delta^{15}\text{N}$ values within an accuracy of $\pm 0.5\text{‰}$ and a reproducibility of better than $\pm 0.3\text{‰}$. Published $\delta^{15}\text{N}$ values from several natural gas wells in East Germany⁶ are in very good agreement with our results. This confirmation of our results allows us to draw the important conclusion that no significant isotopic shifts have occurred, even during a gas production period of almost two decades. In contrast, differences were discovered between published¹⁻⁵ and reanalyzed $\delta^{15}\text{N}$ values in natural gases from reservoirs in West Germany. A comparison of these literature data and our measurements (Table 2 and Figure 9) reveal the following trends:

- (1) All $^{15}\text{N}/^{14}\text{N}$ ratios measured in the BGR laboratory are larger than the published values.
- (2) For gases with a N₂ content of more than 20 vol %, the difference is constant at about 5‰, and thus a correction can be applied.
- (3) The deviation for natural gases with a nitrogen content less than 10 vol % is as much as 30‰. Since the scatter is rather large, no acceptable correction seems to be possible.

Although it was only possible to redetermine selected nitrogen isotope data, we draw the following conclusions: Since all of the published data were measured in the same laboratory at the University of Braunschweig (the analytical procedure is described by Behrens et al.¹¹), analytical problems in that laboratory may be responsible for the isotopic offset. The

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(18) Kettel, D. *Erdöl, Kohle, Erdgas, Petrochem.* **1982**, *35*, 557-559.

values in the above-named literature, as well as the relevant secondary literature,^{17,18} should be used with care.

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