A simple new method for the determination of ammonium isotopes by gas chromatography-mass spectrometry

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Supporting Information Text

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1.1 GC operating conditions

We used a BD-5MS (30m×0.25mm×0.25um) elastic quartz capillary column. The carrier gas was helium and the carrier gas flow rate was 1.0 ml/min. The instrument inlet temperature is 280 °C. The temperature of the column oven is 40 ° C, hold 2 min, 5 ° C / min to 150 ° C, hold 0 min, 40 ° C / min to 260 ° C, hold 5 min.

1.2 Mass spectrometer operating conditions

The instrument is connected to an electron ionization source (EI). The ion source temperature was 280 ° C and the ion transmission line temperature was 280 ° C. The ionization energy is 70eV, and the scanning mode is full scan. The qualitative and quantitative ion selection is shown in Table 1.

Table 1 characteristic ion for target compound

Compound	Retention time(min)	Secondary Ion	Primary ion

$(CH_2)_6{}^{14}N_4$	20.33	85,112	140
$(CH_2)_6{}^{15}N_4$	20.33	87,115	144

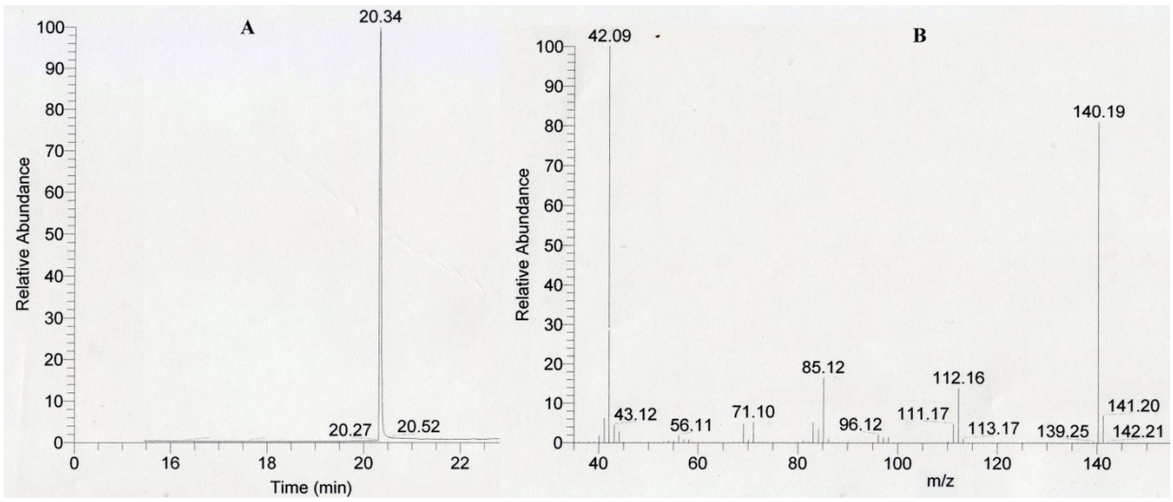

Figure 1 Gas chromatogram(A) and mass spectrum(B) of the $(CH_2)_6{}^{14}N_4$

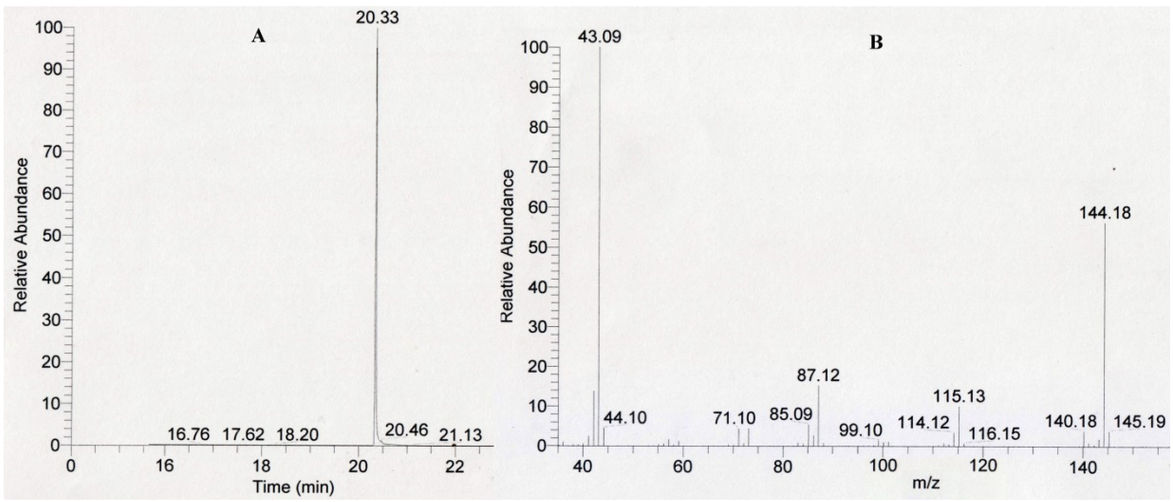

Figure 2 Gas chromatogram(A) and mass spectrum(B) of the $(CH_2)_6{}^{15}N_4$

1.3 Experimental accuracy

We applied this newly developed method to samples containing different concentrations of NH_4^+ at $\delta^{15}N$. 50μmol$(^{14}NH_4)_2SO_4$ and $(^{15}NH_4)_2SO_4$ was added to distilled water and the standard deviation was calculated (repeated operation 6 times)

Table2 Our method has a detection accuracy of $\delta^{14}N/\delta^{15}N$

Serial number	$\delta^{14}N$(μmol)	SD（n=6）（%）	$\delta^{15}N$(μmol)	SD（n=6）（%）
1	41.4	8.46	45.2	6.43
2	42.4		44.0	

3	43.8		44.3	
4	42.7		43.8	
5	45.0		43.8	
6	41.4		46.7	

Table3 The isotope ratio mass spectrometry method has a detection accuracy of $\delta^{15}N$

Serial number	$\delta^{15}N$(μmol)	SD（n=6）（%）
1	45.2	5.2
2	46.4	
3	44.4	
4	45.5	
5	44.1	
6	45.1	

Table4 ultraviolet spectrophotometry method has a detection accuracy of ammonia nitrogen

Serial number	$\delta^{14}N$(μmol)	SD（n=6）（%）
1	47.7	2.9
2	46.4	
3	47.8	
4	47.1	
5	47.4	
6	47.0	

2 GasBench-IRMS Online Continuous Analysis of Nitrogen Isotope

2.1 Instrument configuration:

GasBench: CombiPAL autosampler from CTC Analytics, Switzerland; Pora PlotQ chromatographic column (30m×0.32 mm×20Lm) from Agilent, USA; constant temperature sample tray; acid pump. Delta V Advantage detector (Thermo Finnigan, USA): Highly sensitive electron bombardment ion source, 3kV ion transmission system

2.2 Analytical method:

The first is the sequential movement of the flush/fill needle along the GC PAL autosampler arm. The second is the emptying process for 420s of He gas (purity>99.999%, flow rate 100 mL/min) for each closed headspace sample bottle, the purpose of which is to remove the air in the bottle. The third is to collect 1ml of sample gas and inject it into the test sample bottle, and add a loop (100ul) to inject the sample through the PAL autosampler. The mixed gas of high-purity helium, nitrogen and other gas impurities is separated and passed through a gas chromatographic column at 70°C. Then it enters the Delta V detector (Thermo Fisher) and is bombarded by a high-energy electron beam for ionization. After an accelerating electric field, different mass-to-charge ratios are separated into different ion beams, which enter the receiver and convert them into electrical signals to determine the nitrogen isotope ratio.

The $\delta^{15}N_{sample}$ is used as a reference standard, and the $\delta^{15}N_{sample}$ is calculated according to the following formula:

$$\delta^{15}N(\%) = \left[\frac{R\left({}^{15}N/{}^{14}N_{sample}\right)}{R\left({}^{15}N/{}^{14}N_{air}\right)} - 1 \right] \times 1000$$

R ($^{15}N/^{14}N_{air}$) is the ratio of nitrogen isotope abundance of nitrogen in the air. The analytical accuracy of the $\delta^{15}N_{sample}$ is ±0.2‰.