MASS SPECTROMETRIC DETERMINATION
OF THE NITROGEN-15 CONTENT
OF DIFFERENT EGYPTIAN FERTILIZERS

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Different nitrogen fertilizers produced in Egypt were analyzed mass-spectrometrically for their $^{15}$N content. The results indicate that nitrate fertilizers are relatively enriched in $^{15}$N compared with ammonium fertilizers. The isotopic fractionation of nitrogen encountered in the production processes of fertilizers are discussed.

Introduction

The increased use of artificial nitrogen fertilizers leads to accumulation of nitrate in ground and surface waters and disturb the natural equilibrium of nitrogen cycle, which was balanced before the intervention of mankind through industrial nitrogen fixation. The production of artificial nitrogen fertilizers has been greatly increasing in the last few years and is approximately doubled every six years.1

By chemical analysis methods it is possible to detect the increase of nitrate in water without the knowledge of the source of pollution. However, if there are some characteristic variations of the $^{15}$Nitrogen content of soil — derived nitrate, and nitrate derived from nitrogen fertilizers, it may be possible to identify fertilizer contribution to water pollution.2,3

The purpose of this study is to determine the $^{15}$N content of different nitrogen fertilizers produced in Egypt. This will be the first step in a series of investigations including the $^{15}$N content of waters and soils as well as isotope kinetic studies of the transformations of artificial nitrogen fertilizers in soils.

Experimental

Representative fertilizer samples were collected from different factories in Egypt. The main nitrogen fertilizers produced are: ammonium nitrate, calcium nitrate and urea.
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The method of chemical separation of ammonia and nitrate is similar to that of BREMNER et al. Ammonia is first separated by steam distillation under alkaline conditions and collected in dilute sulfuric acid and back titrated with dilute sodium hydroxide. Devarda alloy is then added to reduce nitrate to ammonia which is processed as above. The ammonium sulfate solutions produced are adjusted to pH 3 by sulfuric acid and evaporated to dryness in a rotary vacuum evaporator.

In order to analyze nitrogen isotopically in the mass spectrometer, it is necessary to convert ammonium sulfate quantitatively to nitrogen gas. This is accomplished by oxidation of ammonium sulfate under vacuum with a lithium hypobromite solution. The details of the vacuum conversion apparatus are described elsewhere.

The mass spectrometer used was a VG Micromass 602 D with a double collector and ratio integrator. Nitrogen gas samples were measured against an air standard, which is freed from oxygen by heated copper. The difference in isotope content of the sample and air standard is expressed as $\delta^{15}N\%o$ defined according to the following equation:

$$\delta^{15}N\%o = \frac{(^{15}N/^{14}N)_{sample} - (^{15}N/^{14}N)_{air}}{(^{15}N/^{14}N)_{air}} \times 1000$$

The $\delta^{15}N$ values reported are the averages of six determinations of the ratio of masses 29 ($^{14}N^{15}N$) and 28 ($^{14}N^{14}N$). Prior to each series of measurements a standard air nitrogen sample was introduced at the same pressure on both sides of the introduction system of the mass spectrometer and the difference in isotopic composition was measured. This difference is always less than 0.1% indicating that no isotopic fractionation is occurring in the mass spectrometer. The mean reproducibility of the chemical conversion process is $\pm 0.2\%o$ $^{15}N$.

Table 1 shows an example of the method of calculation of the $\delta^{15}N$ value and the standard deviation. It is noted that the mean of consecutive readings of column A is incorporated into and shown in column B. This method of calculation takes into consideration the linear drift in the isotope ratio during a run due to changes in mass-spectrometric characteristics or sample depletion for example.

Major Peak sample = major peak reference $= 5 \times (5 \cdot 10^{-9})$ Amp.

$$\delta (\text{NH}_2^+ - ^{15}N) = \frac{-2060 \times 1000}{420381} = -4.9\%o$$