CALIBRATION OF AN EMISSION SPECTROMETRIC ANALYZER MEASUREMENT OF ^{15}N ABUNDANCES

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INTRODUCTION

Non-radioactive tracers are very important for agricultural, biological, chemical and medical research and ^{15}N is not the exception. In order to be able to measure ^{15}N abundances, the INGEIS (Geochronology and Isotopic Geology Institute, Buenos Aires, Argentina) is making an effort to put in operation Jasco NA-1 Analyzer that has been out of service for several years.

Basic research and data compilation for the development of the experimental techniques in which is based this paper where introduced by Fielder and Proksch (1975) and Faust *et al* (1987). Latest techniques on ^{15}N measuring can be reviewed in Boyd (2004) and Toyoda and Yoshida (2004).

JASCO NA-1 ANALYZER

The equipment is an Emission Spectrometric Analyzer made by the Japan Spectroscopic Company and it is designed for the exclusive purpose o determining concentrations of heavy nitrogen.

It works with gas samples with very low quantities of nitrogen (pressures of 3 to 5 mm Hg) on discharge tubes (quartz or Pyrex capillary tubes). When the nitrogen molecules are excited to the luminescence, a number of emissions band spectra are obtained. Of these, 2977, 2983 and 2989 Å bands corresponding to $^{28}N_2$, $^{14}N^{15}N$ and $^{15}N_2$ molecules respectively, most suited for the spectrometry are used for determining ^{15}N ratios. The excitation emission of nitrogen molecules is induced by applying high frequency wave to a discharge tube filled with N_2 gas (electrodeless discharge). The high frequency oscillator for this instrument is of 13.56 MHz, 300W output, and the discharge with a Tesla coil specially developed for this purpose and provided by JASCO CO.

After amplification and multiplication of the signal the amplitude data output is done trough a strip chart.

EXPERIMENTAL TECHNIQUE

Once the equipment is turned on and all the basic functions of the instrument checked, the atomic %^{15}N measuring started. In the first experiments, a problem appeared in the analogical data output, and the peaks where plotted incompletely (Fig. 1). This problem was solved by adjusting de timer switch that determines when the equipment is measuring $^{28}N_2$ and $^{29}N_2$ + $^{30}N_2$ molecular abundances.

Nine standard samples, bought with the equipment, where used for the calibration procedure. In Table 1 the atomic %^{15}N of the standard samples is compared with the atomic %^{15}N measured.

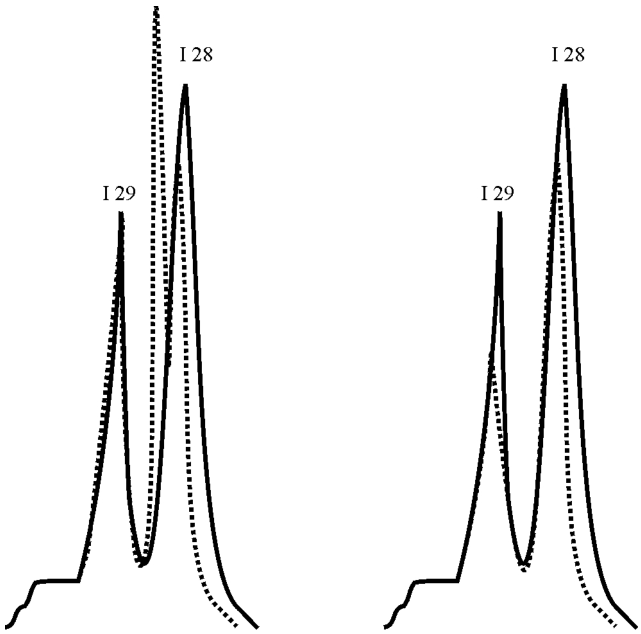

Figure 1. Correction for wrong time difference between the measured molecular quantities of $^{28}N_2$ and $^{29}N_2$ molecular quantities measuring can produce. Wrong measures are plotted as dotted line; correct measures are plotted as continuous line.

INACCURACY CORRECTION

The inaccuracy of the measures had been corrected by cubic spline interpolation. The spline is a sum of cubic polynomial functions that work in a range of data (known ^{15}N concentrations in our case). A description of the cubic spline interpolation theory is in Burden and Faires (2001). These functions had been calculated with Octave Software (free Linux clone of MatLab Software).

A plot of the measured value of ^{15}N concentrations and the inaccuracy is given in Figure 2. The inaccuracy % needed to correct the measured value in the range of the standard samples can be estimates form this plot.

NEW SAMPLES PREPARATION

A procedure to prepare nitrogen gas samples from organic and mineral materials using the Dumas method is being developed by the technical staff at INGEIS.

CONCLUSSIONS

We conclude that the atomic abundances of nitogen isotopes can be measured by emission spectrometry at INGEIS, Buenos Aires. The cubic spline interpolation is an appropriated method for the development of an inaccuracy correction like the one needed for the Jasco NA-1 Analyzer needed. At high ^{15}N concentrations the agreement between the measured values and the recommended values for standard materials is satisfactory.

The objectives on the immediate future of this technique team is to prepare samples of known ^{15}N concentration using the Dumas Method, and a new digital output of the data should be connected in order to reduce the inaccuracy of the measure produced by the analogical strip chart output.

AKNOWLEDGEMENTS

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STANDARD		MEASURED VALUES (ATOMIC %^{15}N)					AVERAGE MEASURED VALUE (ATOMIC %^{15}N)	INACCURACY (%)
SAMPLE	ATOMIC %^{15}N							
1	**0.366**	0.460	0.447	0.454	0.370	0.457	**0.438**	19.563
2	**0.653**	0.770	0.726	0.775	0.682	0.732	**0.737**	12.864
3	**0.911**	1.050	0.940	0.938	0.908	0.908	**0.949**	4.149
4	**1.500**	1.700	1.550	1.674	1.548	1.674	**1.629**	8.613
5	**2.400**	2.636	2.597	2.594	2.597	2.555	**2.596**	8.158
6	**3.430**	3.710	3.660	3.707	3.564	3.665	**3.661**	6.741
7	**5.330**	5.560	5.460	5.713	5.927	5.469	**5.626**	5.550
8	**9.830**	9.830	9.957	9.898	9.907	9.524	**9.823**	-0.069
9	**24.100**	21.393	21.197	21.393	21.411	21.608	**21.400**	-11.202

Table 1. Recommended and measured ^{15}N concentrations and the corresponding innacuracy % of standard samples.

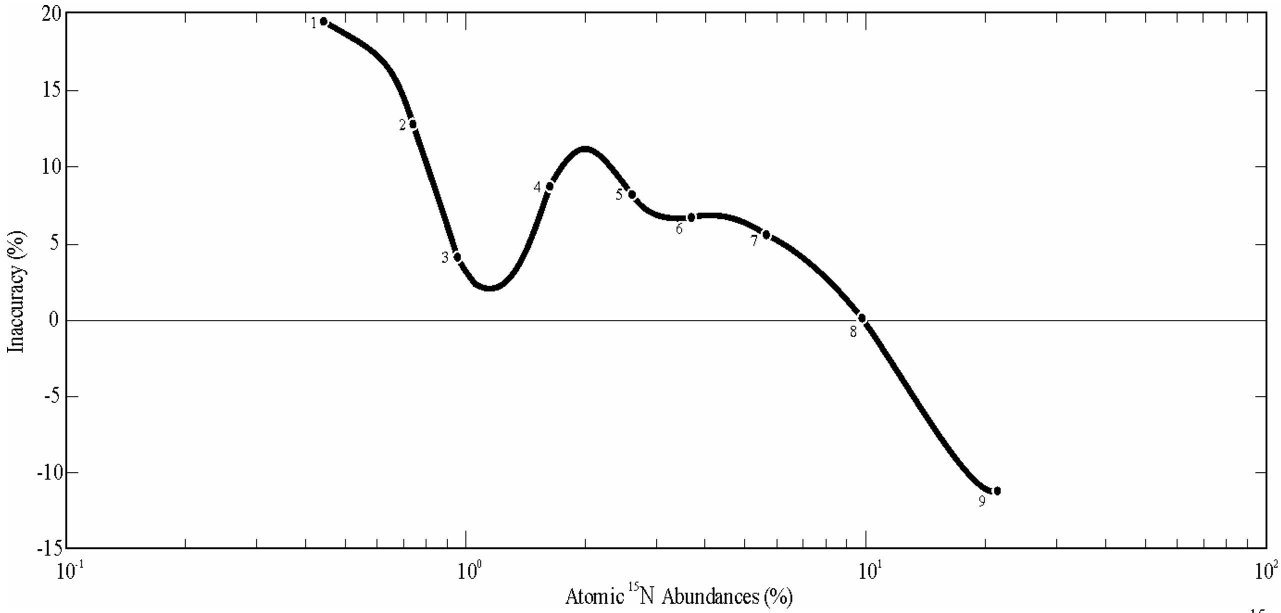

Figure 2. Cubic spline interpolation curve obtained with Octave Software to correct measured values of ^{15}N concentrations. Numbers of the standard samples are plotted. A logarithmic scale is used for better resolution.

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RESUMEN

La calibración de un Analizador de Emisión de Espectrometría fue necesaria para poder medir concentraciones de ^{15}N. Utilizando nueve patrones standard se ajustó el interruptor de tiempo que mide la abundancia molecular de $^{28}N_2$ y $^{29}N_2$ + $^{30}N_2$ para obtener mediciones correctas. Luego se aplicó una interpolación cúbica para corregir el error presentado por las mediciones de los patrones de concentración conocida. En el futuro próximo se realizaran nuevas muestras por medio del método de Dumas y se conectara una salida digital para mejorara los resultados.