

# Automatic and Sensitive Determination of $^{15}\text{N}$ -Abundance in Inorganic Compounds of Aqueous Samples with SPINMAS.



A. Götz<sup>2</sup>, B. Apelt<sup>1</sup>, R. Russow<sup>1</sup>

<sup>1</sup> UFZ - Leipzig - Halle GmbH, Sektion Bodenforschung, Theodor-Lieser-Straße 4, D-06120 Halle, e-mail: bapelt@bdf.ufz.de  
<sup>2</sup> InProcess Instruments GmbH, Otto-Lilienthal-Str. 19, D-28199 Hansestadt Bremen

## Method

The determination of  $^{15}\text{N}$ -abundance in smallest N-amounts of inorganic compounds like Nitrite and Nitrate is a continuous repeating task in  $^{15}\text{N}$ -tracer studies of biological systems. For nitrite, which is only available in smallest concentrations, there was no practical method known yet. Therefore, a method, based on the principle of Reaction-Continuous-Flow-Mass-Spectrometry (R-CF-MS), was developed, which allows the fast and precise  $^{15}\text{N}$  determination of these compounds in aqueous samples of very small amounts (ng -  $\mu\text{g}$  scale). (Russow 1999)

The Nitrogen of the selected compounds is converted to Nitrogen monoxide (NO) (in a continuous flow-through system). The formed NO will be transported with He as a carrier gas to the mass spectrometer for continuous measurement. [1] To use this method in an automatic routine analysis, an apparatus was developed, which converts by means of special reagents the inorganic Nitrogen compounds of Nitrite, Nitrate, Ammonia and Hydroxylamine into the gases of NO,  $\text{N}_2$  or  $\text{N}_2\text{O}$ , respectively. The whole process is monitored and controlled by a PC. [2]

(SPIN – Sample Preparation of Inorganic N-compounds). The SPIN unit is coupled with a quadrupole mass spectrometer GAM 400 (InProcess Instruments GmbH, Bremen, Germany) for the measurement of the  $^{15}\text{N}$ -abundance of the formed gases. For the automatic sampling, an automatic sample changer, model “222 XL Liquid Handler” from GILSON is used. The GAM 400 provides enough digital output channels to monitor the automatic sample changer. The control of the complete measuring cycle is handled by a PC with specific application software.

## Technical solution

During the development phase different materials had to be tested, in order to withhold the aggressive reaction solution of  $\text{V(III)Cl}_3$  in a HCL acid media.

The optimal material to be found and used since for the double cannula is silver, the material also offers a strong mechanical strength and is corrosion resistant.



Figure 1. SPINMAS automatic coupling with sample changes



Figure 2. SPINMAS coupling with automatic sample changer and quadrupole mass spectrometer

## Results

N-compound	Detection limit [ng N]	Quantitation limit* at	
		a $\geq 1$ At. % [ $\mu\text{g N}$ ] [ $\mu\text{g N/l}$ ]	n.A. [ $\mu\text{g N}$ ] [ $\mu\text{g N/l}$ ]
Nitrite	10	0,1	1
		10	100
Nitrate	50	1,0	5
		200	1000
Ammonium	1000	5,0	20
		500	2000
Hydroxylamine	200	2	10
		200	1000

Table: 1: Detection limit and quantitation limit for the amount and  $^{15}\text{N}$  abundance in Nitrite-, Nitrate- and Ammonium-N for the automatic measuring method SPINMAS.

\* Standard deviation  $\leq 3\%$ , n.A. - Natural abundance  
 The concentration refers to a maximum sample volume of:  
 - 10 ml for Nitrite  
 - 5 ml for Nitrate  
 - 10 ml for Ammonium  
 - 10 ml for Hydroxylamine

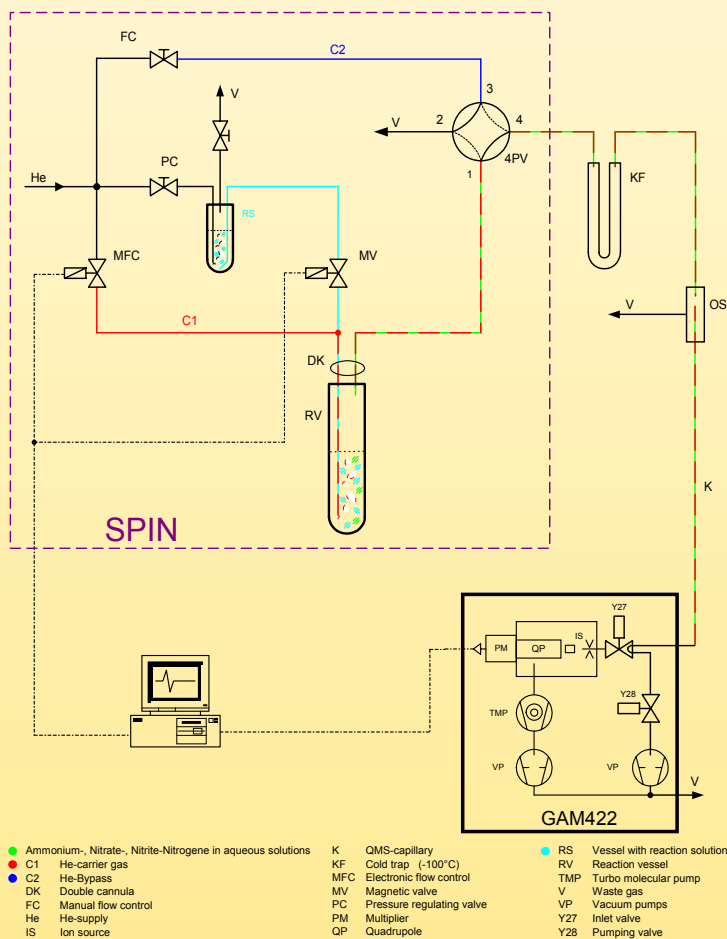


Figure 3. Reaction-Flow scheme of the automatic system SPINMAS

## Advantages

- ☐ The smallest up to date used sample volume containing sufficiently nitrogen in the compound is 0,5 ml.
- ☐ By this method a drastic time saving was achieved in comparison to the classical  $^{15}\text{N}$  determination.
- ☐ The complete measuring cycle for one sample is 10 min.
- ☐ The sample holder can hold up to 70 samples which are measured automatically.

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Literature:  
 [1] Russow, R.: Determination of  $^{15}\text{N}$  in  $^{15}\text{N}$ -enriched nitrite and nitrate in aqueous samples by reaction continuous-flow quadrupole mass spectrometry. Rapid Communication in Mass Spectrometry 13 (1999) 1334-1338  
 [2] Russow, R., Schmidt, G., Fischer, H., Nitschke, W.: Verfahren und Vorrichtung zur automatischen  $^{15}\text{N}$ -Bestimmung von Ammonium-, Nitrit- und Nitrat-Stickstoff in wässrigen Lösungen. Deutsches Patent 197 35 927, Deutsches Patent- und Markenamt, München, erteilt 16.09.1999