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

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Method

The determination of ^{15}N-abundance in smallest N-amounts of inorganic compounds like Nitrite and Nitrate is a continuous repeating task in ^{15}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}N determination of these compounds in aqueous samples of very small amounts (ng - µg 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, N_2 or N_2O, 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}N-abundance of the formed gases. To analyze up to 100 samples (including Blanks, Reference, Calibration) a new robotic system was developed. This uses an innovative purging concept to keep the blank values and air contribution very low for improvement of the detection limits. The Robotic is controlled by a gate program developed by IPI to change automatically between samples. The MS program coordinates sample change and analysis full automatic and includes an innovative safety concept.

Technical solution

During the development phase different materials had to be tested, in order to withhold the aggressive reaction solution of $V(III)Cl_3$ 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

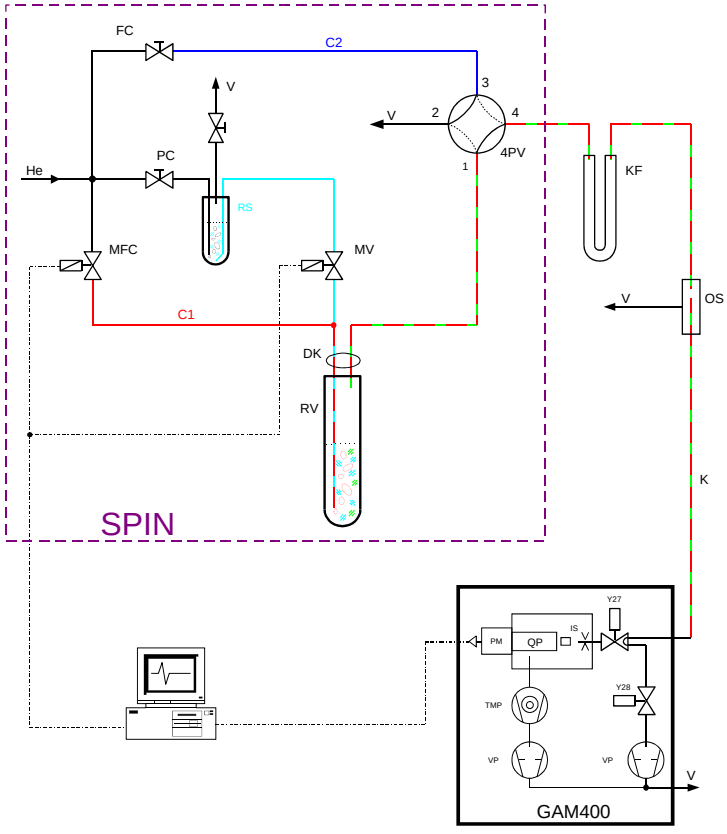
Figure 2. SPINMAS coupling with Robotic System and quadrupole mass spectrometer

Results

N-compound	Detection limit [ng N]	Quantitation limit* at a ≥1 At.% [µg N] [µg N/l]	Quantitation limit* at n.A. [µg N] [µg 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}N abundance in Nitrite-, Nitrate- and Ammonium-N for the automatic measuring method SPINMAS.

* Standard deviation ≤ 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



- Ammonium-, Nitrate-, Nitrite-Nitrogene in aqueous solutions
- C1 He-carrier gas
- C2 He-Bypass
- DK Double cannula
- FC Manual flow control
- He He-supply
- IS Ion source
- K QMS-capillary
- KF Cold trap (-100°C)
- MFC Electronic flow control
- MV Magnetic valve
- PC Pressure regulating valve
- PM Multiplier
- QP Quadrupole
- RS Vessel with reaction solution
- RV Reaction vessel
- TMP Turbo molecular pump
- V Waste gas
- VP Vacuum pumps
- Y27 Inlet valve
- Y28 Pumping valve

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}N determination.
- The complete measuring cycle for one sample is 10 min.
- The sample holder can hold up to 100 samples which are measured automatically.

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Literature:

[1] Russow, R.: Determination of ^{15}N in ^{15}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}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