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Automatic Determination of Content and ^{15}N abundance of Total Dissolved Nitrogen in Watery Samples and Soil Extracts by TOC Analyser-Mass Spectrometer Coupling

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The standard method for determining the ^{15}N abundance of total dissolved nitrogen (TDN: org. N + $\text{NH}_4^+\text{-N}$ + $\text{NO}_3^-\text{-N}$) in aqueous samples (e.g. soil leachate, sewage, urine) is currently Kjeldahl digestion followed by steam distillation or diffusion to isolate the ammonium, and then ^{15}N measurement using IRMS (Bremner & Mulvaney, 1982, Brooks et al., 1989). However, this technique is both time-consuming and laborious. Using elemental analyser-IRMS coupling is impossible owing to the required sample volumes of ≥ 0.5 ml. A solution to this problem emerged with the availability of TOC analysers to determine the total dissolved carbon and nitrogen in aqueous samples. The HighTOC analyser (Elementar Hanau, Germany), which catalytically oxidizes the sample's total nitrogen with a high, constant yield to form nitrogen monoxide (NO), appeared particularly suitable. As ^{15}N determination of NO using mass spectrometry had already proved successful (Russow & Stevens, 1996, Sich & Russow, 1999) online coupling with a suitable MS via the combustion product NO ought to enable the rapid, automatic ^{15}N determination of the total dissolved nitrogen in a sample with sufficient sensitivity and accuracy. The Quadrupol-MS ESD 100 (InProcess Instruments Bremen, Germany) proved to be a suitable mass spectrometer. It is known that oxygen, necessary for a sufficient combustion, has a big impact on the detection of the relevant masses 30 and 31 by the mass spectrometer. This causes changes in the background of the MS record which lead to unacceptable incorrect ^{15}N determinations. This problem could be solved by an indirect coupling of the TOC analyser to the QMS via a cryotrap immersing into liquid nitrogen working after the "trap and flash" principle (Sich & Russow, 1998). The coupling of the instruments described was found in numerous measurements of standard and real samples to provide a workable method. The detection limit is about 2 μg of nitrogen, corresponding to an N concentration of 0.07 mg/l in a maximum dosage volume of 3 ml. Depending on the N concentration, ^{15}N abundances starting from 0.5 at.% can be measured with the required precision of better than 3% (simple standard deviation). For example, measuring the abundance of 0.5 at.% requires about 50 μg N, whereas as of 1 at.% only about 5 μg N is needed per analysis.

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Sulfur isotope distribution at Bleiberg lead-zinc deposit (Austria) and its genetic implication.

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Bleiberg (Carinthia, Austria) is the Alpine type deposit (ATP) of the low-temperature carbonate-hosted lead-zinc mineralisations. The ores are hosted by 350m Ladinian to Carnian platform carbonates. Genetically related lead-zinc deposits are found in Mežica (Slovenia) and Raibl (Italy). These deposits are located along the Periadriatic lineament, which separates the Austroalpine from the Southalpine tectonic unit. Mining ceased at the end of the 20th century. With a total production of 2.4 Mio t Pb+Zn, the deposit of Bleiberg is the largest deposit of the ATP.

The genesis of this deposit is discussed controversially. A Carnian sedimentary-sydiagenetic origin (Brigo et al. 1977, Schroll 1996) is opposed against a (MVT) model of migrating brines during post-Norian (Jurassic) age (Zeeh et al. 199?, Kuhleemann et al. 2002).

The interpretation of the sulfur isotope distribution in the Alpine ore district is an efficient contribution to evaluate these contrary models.

The Bleiberg deposit is characterized by a complex mineralisation, distributed in six ore horizons. In spite of the uniformity of the ore mineralization, differences in mineralogy, trace element geochemistry of sphalerite, and sulfur isotopes of sulfides are observed in dependence of the stratigraphic position and the structural setting of the mineralisation (Table 1). Geochemical data, e.g. Ga/Ge-ratio of sphalerite, indicate a leaching temperature around 100°C. The burial temperature of Carnian sediments at Bleiberg is estimated with ca. 130°C (Rantitsch 2001).