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Short Report

Application of a Purge-and-Trap System for Fixed-NH_4^+ Determination by Matrix Interference Free Ion Chromatography in Oil Reservoir Rocks

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É proposto um método para determinação de NH_4^+-fixo utilizando um sistema de arraste imerso em um banho ultrassônico para extração de NH_3 e cromatografia de íons para determinação de NH_4^+. O método é mais rápido, simples e sensível (LOD = 4,4 µg g^{-1} NH_4^+) que o método clássico Kjeldahl.

A method for fixed-NH_4^+ determination using a system immersed into an ultrasonic bath for NH_3 extraction and ion chromatography for NH_4^+ determination is proposed. The method is faster, simpler and more sensible (LOD = 4.4 µg g^{-1} NH_4^+) than the classical Kjeldahl method.

Keywords: fixed-ammonium, sandstone, ion chromatography, ultrasound-assisted purge-and-trap system.

Introduction

The determination of fixed-NH_4^+ in sedimentary rocks has been applied in geochemical studies for exploration purposes, especially in the oil industry.[1-8] The studies are based on a conceptual model of NH_4^+ fixation in oil source rocks during the burial diagenesis. This model explains why larger relative quantities of NH_4^+ are fixed in transformed authigenic clays (*e.g.* illite, illite-smectite or illite-smectite-vermiculite), in sandstones and is generally consistent with depth-diagenesis schemes for clay minerals and generation of hydrocarbons from the thermal maturation of organic matter. Relative changes in fixed-NH_4^+ concentrations serve as indicators of hydrocarbons formation or may indicate their pathways during the migration from source beds to reservoirs.[2,4]

The wet analytical methods for fixed-NH_4^+ determination have been carried out in three steps: (*i*) previous removal of inorganic exchangeable-N with an extractant (*e.g.*, 2 mol L^{-1} KCl), followed by the organic-N removal with an oxidant reagent (*e.g.*, KOBr or NaOCl) [2,4,9] or removal of exchangeable-N and organic nitrogen species with 1 mol L^{-1} KOH; (*ii*) release fixed-NH_4^+ by destruction of the silicates with a HF and HCl mixture[1,10] and (*iii*) Kjeldahl steam distillation.[2,4,9,10] The ammonium concentration in the solution obtained after the distillation has been determined by titrimetric;[2,4,10] or colorimetric methods.[11] A limit of detection (LOD) of 56 mg kg^{-1} for fixed-NH_4^+ determination in sedimentary rocks was reported.[2]

A simplified purge-and-trap system for NH_3 extraction was recently used for total nitrogen determination.[12] This system presented many advantages, among them, the matrix interference elimination, mainly Na$^+$, which was necessary for NH_4^+ determination by ion chromatography. In the present work, this system was proposed for fixed-NH_4^+ determination. All results were compared with those obtained with the classical Kjeldahl method. Sandstones from Brazilian oil reservoirs with different fixed-ammonium were analyzed.

Experimental

Apparatus and operating conditions

An US-bath model USC-1400 from Unique (Indaiatuba, SP, Brazil) with a power of 120 W, frequency

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of 40 kHz and volume of 3 L to convert the released-NH_4^+ into NH_3 vapor was used. A water-bath model 304-149 from Quimis Aparelhos Científicos (Diadema, SP, Brazil) was used to remove exchangeable-NH_4^+ and organic-N from the samples by the proposed and comparative methods. A CELM centrifuge model LS-3 (Barueri, SP, Brazil) with 3200 rpm of speed was used. A Metrohm chromatography system (Herisau, Switzerland) with a dialysis membrane model 788, a vacuum degasser model 837 and a conductivity detector model 819 were used for NH_4^+ determination. Integrated areas were used to quantify ion signals. Ammonium separation was carried out in a METROSEP C2 250/4.0 column (Herisau, Switzerland) with 7.0 μm particle diameter. The flow-rate of the eluent (4.0 mmol L^{-1} tartaric acid/0.75 mmol L^{-1} 2,6-pyridinecarboxylic acid) was kept at 1.0 mL min^{-1}; the column temperature was 35 °C and the running time was 15 min. The sample loop volume was 20 μL. The mineralogical characterization of all samples was carried out by X-ray diffraction (XRD, powder method) using a Bruker diffractometer model AXS D5005 equipped with Goeble mirror. Working conditions were: CoK_α monochromatic radiation, 40 mA and 35 kV. Samples were run at a speed of 0.02 degree s^{-1}. Qualitative mineralogical determination was estimated with Diffrac^{Plus} software.

Reagents, standards and samples

All chemicals used were of analytical grade. The water was purified with a reverse osmosis system model Elix 5 and deionized Milli-Q from Millipore Indústria e Comércio Ltda. (Barueri, SP, Brazil). The following solutions were used: 1 mol L^{-1} KOH, 7.5 mol L^{-1} HF, 1 mol L^{-1} HCl, 0.1 mol L^{-1} HCl and 1000 mg L^{-1} NH_4^+ (NH_4Cl) stock standard solution. The intermediate standard solutions were daily prepared. Sandstones from Brazilian oil reservoirs with different fixed-NH_4^+ concentrations were analyzed.

Removal of exchangeable-N and organic-N

An aliquot of 25 mL of 1.0 mol L^{-1} KOH was added to a 50 mL polypropylene centrifuge tube containing 0.2 g of sample, pre-treated as Pontes *et al.*[12] described. The mixture was then heated at 80 °C for 8 h in a water-bath. After the mixture reached room temperature, the phases were separated by centrifugation. The supernatant was discarded, and the residue was washed three times with 5 mL of 1 mol L^{-1} KOH and finally with water. This procedure was adopted for the comparative and proposed methods.

Release of fixed-NH_4^+

An aliquot of 10 mL of a mixture containing 7.5 mol L^{-1} HF and 1.0 mol L^{-1} HCl was added to the polypropylene centrifuge tube containing the residue. The mixture was heated in a water-bath at 80 °C for 12-16 h, until it was almost dry. This procedure was adopted for both comparative and proposed methods.

Released-NH_4^+ determination by the comparative method

After the mixture has reached the room temperature, it was transferred to a polypropylene distillation tube of the Kjeldahl system. Then, NH_3 was distilled, collected as NH_4^+ and determined by the indophenol colorimetric method.[12]

Ammonia extraction by the US-assisted purge-and-trap system (proposed method)

The flow diagram for the NH_3 extraction by US-assistance was similar to that showed by Pontes *et al.*[12] with the following modifications: all tubes were made of Teflon and the manifold were of polypropylene; the dimensions of the reaction tube and the NH_3 collection tube were 2.7 cm i.d. and 12 cm length; the dimensions of the U tube were 0.3 cm i.d. and 13 cm length; the manifold (0.6 cm i.d.) had six tips to connect six sets and one more tip to connect the vacuum pump. The polypropylene tube containing the released-NH_4^+ in solution was connected to the U tube, and then the procedure was the same as Pontes *et al.*[12] described.

Results and Discussion

Analytical results

The working concentration of NH_4^+ was in the range of 100 to 800 μg L^{-1}; the linear regression of the analytical curve gave a slope of 0.1863 mV s L μg^{-1} and the correlation coefficient of the calibration curve was higher than 0.99. The blank measurement was 13 ± 2 μg L^{-1} NH_4^+ (n = 10). The LOD was 4.4 μg g^{-1} NH_4^+. It was calculated from the equation LOD = $3S_{BL}/b$, where S_{BL} was the standard deviation of ten blank concentration measurements and *b* was the slope of the calibration curve. The relative standard deviations (RSD) were lower than 11% (n = 3). Good agreement was found between the results of fixed-NH_4^+ obtained by the proposed method and those obtained by the classical Kjeldahl method (Table 1). The sample diffractograms (not shown) indicated the

Table 1. Concentrations (μg g^{-1}) of the fixed-NH_4^+ in sandstone samples obtained by the classical and proposed methods (n = 3)

Sandstone sample	Method	
	Classical	Proposed
1	378 ± 14	365 ± 9
2	86 ± 6	75 ± 7
3	127 ± 14	108 ± 11
4	519 ± 43	492 ± 55
5	447 ± 12	431 ± 39

presence of illite, which probably was responsible by the NH_4^+ fixation.

Conclusion

The simplified method for ammonia extraction is faster and simpler than the classical Kjeldahl steam distillation method. The limit of detection (LOD) was 4.4 μg g^{-1} NH_4^+. The relative standard deviations (RSD) were lower than 11% (n = 3).

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