A gas-diffusion flow injection method coupled with online solid–liquid extraction for the determination of ammonium in solid samples

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ABSTRACT

A simple, rapid and reliable gas-diffusion flow injection (GD-FI) method for ammonium determination in building materials has been developed. It is based on leaching ammonium from a ground solid sample into an alkaline solution with subsequent ammonia gas generation. Ammonia is then transported in a nitrogen stream to the GD cell of the FI system where it is absorbed into its acceptor solution containing a mixture of the acid–base indicators cresol red and thymol blue. The maximum increase in the absorbance of the acceptor solution at 580 nm is related to the ammonium concentration in the solid sample. The proposed method is characterized by a linear concentration range of 0.1–5.0 mg NH_4^+ kg^{-1}, a limit of detection of 8 μg NH_4^+ kg^{-1} and a sample throughput of 10 h^{-1}. A successful application of this method for the determination of ammonium in building materials such as concrete, cement and sand is reported.

1. Introduction

In recent years considerable attention has been devoted to the problem of ammonia emission in the indoor space of buildings and lodgings [1]. The main sources of this emission are different concrete additives containing urea, which are used to improve the technical characteristics of concrete at low temperatures. But, as soon as the temperature and humidity increase, urea in these additives starts to decompose and this causes the release of ammonia into indoor spaces [1]. The source of ammonia is provided by the decomposition of urea in aqueous medium to ammonium cyanate (NH_4CNO) where the cyanate anion can further decompose to ammonium and carbonate [2]. The presence of ammonia at high concentrations in residential and office spaces will make them unsuitable for habitation or work. Therefore, it is essential to develop methods for assessing the potential of concrete and other building materials to emit ammonia.

Numerous methods for the determination of ammonia and the ammonium ion have been developed and they employ detection techniques such as spectrophotometry [3–8], spectrofluorometry [9–11], conductometry [12,13], chromatography [14,15], capillary electrophoresis [16–18], and potentiometry [19].

The spectrophotometric determination of ammonia/ammonium in both batch-wise and flow analysis methods is frequently based on the Berthelot reaction or its modifications where phenolate is replaced with less toxic reagents (e.g. salicylate) [20–22].

This approach has been applied earlier by us in the development of an automatic flow analysis method for the determination of ammonium in concrete samples [23]. This method is based on headspace single-drop micro-extraction of ammonia followed by stepwise injection spectrophotometric analysis (SWIA-HSDME) based on the Berthelot reaction. The obvious drawback of this method is its low sample throughput (4 h^{-1}) due to the lengthy duration of both the extraction process and the analytical color reaction.

Spectrophotometric detection of ammonia/ammonium in flow analysis involving the use of acid–base indicators has been successfully applied as an alternative to the Berthelot reaction. While this approach is cheaper in terms of the reagents used, produces results much faster and does not need elevated temperatures, its implementation requires the introduction of a highly selective online GD [24–26] or pervaporation [27–29] separation step prior to the analytical detection. In both membrane separation techniques the sample is introduced into a donor stream where a volatile or semi-volatile analyte or analyte that can be converted chemically into volatile species is separated from the sample matrix containing interferents by transferring it across a hydrophobic porous membrane into a static or flowing acceptor solution in direct contact with the membrane and containing suitable acid–base indicators [24]. In

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GD separation the donor stream is also in direct contact with the membrane while in pervaporation separation there is an air gap between the membrane and the donor stream which prevents potential deterioration in the membrane permeability by surfactants, corrosive compounds or micrometer size particulates in the sample matrix.

This paper reports on the development and validation of a GD-FI method for the determination of ammonium in building materials such as concrete, cement and sand which is faster and simpler than the SWIA-HSDME [23] mentioned above.

2. Experimental

2.1. Solution preparation

All chemicals were of analytical reagent grade. Deionized water (18.2 MΩ cm, Millipore, France) was used for the preparation of all solutions. The acid–base indicator stock solution contained 0.05% and 0.15% (w/v) cresol red (Sigma-Aldrich) and thymol blue (Sigma-Aldrich), respectively [29]. The acceptor solution was made daily by 50 fold dilution of the acid–base indicator stock solution and its pH was adjusted by drop-wise addition of 0.01 M NaOH (Chem Supply) solution.

The ammonium stock solution (100 mg NH_4^+ L^{-1}) was prepared by dissolving the corresponding amount of NH_4Cl (Sigma-Aldrich) in 0.1 M HCl solution. The ammonium working solutions were prepared immediately before the experiments by appropriate dilution of the ammonium stock solution. Stock solutions (100 mg L^{-1}) of methylamine (Sigma-Aldrich) and ethylamine (Sigma-Aldrich) contained 0.1 M HCl and were stored refrigerated (4 °C).

Sulfuric acid (Chem Supply) was used for cleaning-up of the nitrogen carrier gas from traces of gases with basic properties such as ammonia.

2.2. Equipment

2.2.1. GD-FI system

The experimental GD-FI system, shown in Fig. 1A, was linked to a nitrogen line, used for purging ammonia from the alkaline sample suspension during ammonium leaching. Nitrogen was first passed through a scrubber containing 0.5 M H_2SO_4 solution for the removal of traces of ammonia or other basic gases. Traces of acidic gases (e.g. CO_2) were absorbed in the alkaline sample suspension. The GD cell (Fig. 1B) consisted of two Perspex disks (i.d. 60 mm), held together by stainless steel ring clamps and four stainless steel bolts. Elliptical shape donor/acceptor chambers were machined in the blocks with major and minor axes of 30 and 5 mm, respectively. The depth of both the donor and acceptor chambers, separated by a hydrophobic porous membrane, was 1 mm. Four different types of polytetrafluoroethylene (PTFE) and polyvinylidenefluoride (PVDF) membranes were examined in this research, i.e. PTFE plumber's tape (thickness ≤ 0.2 μm), PTFE bonded to polyethylene support (Fluoropore, Millipore, 0.2 μm), PVDF (SureVent, Millipore, 0.1 μm), and PVDF (Durapore, Millipore, 0.22 μm). The nitrogen flow, which purged ammonia from the sample suspension in the thermostated at 20 °C suspension reservoir, immersed in an ultrasonic bath (UNISONICS, Australia), was directed through the donor chamber of the GD cell to the ambient atmosphere. The nitrogen flow rate was monitored using a flow-meter (Aalborg Instruments & Controls, USA). The acceptor solution was propelled through the acceptor chamber of the GD cell using a peristaltic pump (VS4-10R-Midi, Watson-Marlow), equipped with Tygon® pump tubing. The acceptor stream then passed through the flow-through cuvette (10 mm optical path length, Starna, UK) of the spectrophotometric detector (Novaspec II, Amersham) set at 580 nm and connected to a PC
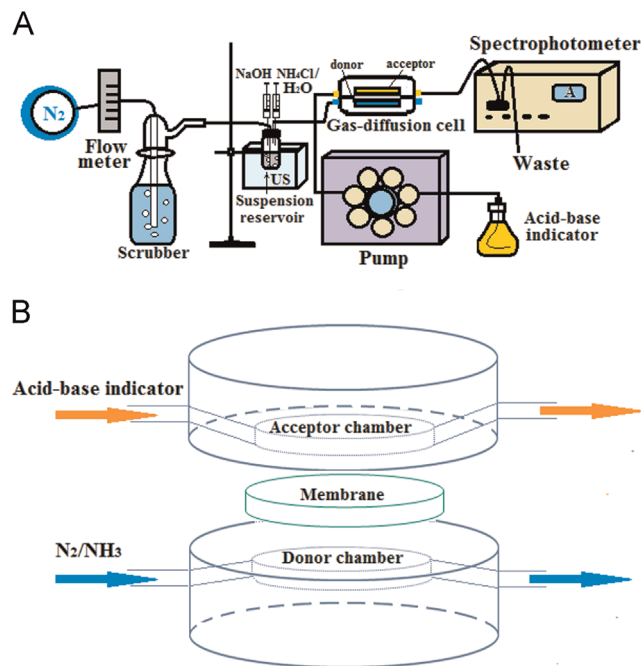

Fig. 1. Schematic diagrams of the proposed GD-FI system (A) and its GD cell (B).

equipped with an NI USB-6009 (National Instruments, USA) data acquisition card and running a home-written in LabVIEW 8.5 (National Instruments, USA) data acquisition program. Connecting tubing (0.8 mm i.d.), made of PTFE, was used in the construction of the GD-FI system.

2.2.2. Other equipment

A gas chromatograph–mass spectrometer (GC–MS) (QP2010Ultra, Shimadzu, Japan) was used to determine the presence of volatile amines in the concrete samples analyzed by the proposed GD-FI method.

2.3. Experimental procedure

2.3.1. GD-FI procedure

The ground solid sample (0.20 ± 0.02 g, fraction 60–80 μm) was placed in a capped 1 mL glass vial, acting as the suspension reservoir, which was located in an ultrasonic thermostating bath. Then 0.3 mL of 2 M NaOH and 0.1 mL of water or ammonium standard solution (in case of calibration or recovery experiments) were injected manually through the cap septum using two hypodermic syringes (Fig. 1A) resulting in the generation of molecular ammonia. This was followed by 5 min of purging the suspension/solution with nitrogen, delivered through a syringe needle piercing the cap septum and connected to Tygon tubing linked to the scrubber (Fig. 1A). During purging, the acceptor solution in the acceptor chamber of the GD cell remained static to allow the accumulation of ammonia diffusing across the hydrophobic porous membrane from the nitrogen stream passing through the donor chamber. These processes led to a change in the color of the mixed acid–base indicator acceptor solution located in the acceptor chamber of the GD cell. After 5 min stop-flow time the acceptor stream was re-started and a transient absorbance peak was recorded at 580 nm whose maximum was related to the concentration of ammonium in the corresponding sample or standard solution. Nitrogen was passed through the donor line of the GD-FI system for 1 min after each measurement to avoid sample cross-contamination.