



Automated procedure for determination of ammonia in concrete with headspace single-drop micro-extraction by stepwise injection spectrophotometric analysis



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ABSTRACT

A novel automatic stepwise injection headspace single-drop micro-extraction system is proposed as a versatile approach for automated determination of volatile compounds. The system application is demonstrated for ammonia determination in concrete samples. An ammonia gas was produced from ammonium ions and extracted on-line into 5 μL 0.1 M H_3PO_4 to eliminate the interference effect of concrete species on the ammonia stepwise injection spectrophotometric determination. The linear range was 0.1–1 mg kg^{-1} with LOD 30 $\mu\text{g kg}^{-1}$. The sample throughput was 4 h^{-1} . This system has been successfully applied for the determination of ammonia in concretes.

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1. Introduction

A variety of interior conditions may contribute much to the people health. Nowadays, considerable attention has been devoted to the problem of ammonia emission into the indoor space of buildings and lodgings. Depending on the country, the permissible exposure limits of ammonia in air vary from 17 mg m^{-3} to 35 mg m^{-3} [1]. However, the values of daily average maximum permissible concentration of ammonia indoors are much less, for example, 0.02 mg m^{-3} and 0.04 mg m^{-3} in China [GB 50325-2001] and Russia [GN 2.1.6.1338-03], respectively. Residential and office space with high ammonia content are not suitable for life or work. Ammonia is considered to release due to hydrolysis of urea, which may be present in antifreeze additives in wintertime [2]. Therefore, the development of a novel method of ammonia determination appears to be of the utmost importance. It is essential to reveal sources of ammonia emission and to control their quality.

Number of analytical methods, such as spectrophotometric [3–8], electrochemical [9,10], chromatographic [11,12], and capillary electrophoresis [13–15], are used for ammonium content evaluation in various objects. Various flow methods have been

widely applied for the rapid ammonium determination by means of spectrophotometric [16,17], electrochemical [18,19], and fluorimetric [20,21] detection modes.

Berthelot reaction [22] and its various modifications involving the formation of intensely colored indophenol-blue complex have been commonly employed in flow mode. However, the flow spectrophotometric determination of ammonia in samples with complicated matrices requires the separation of ammonia from sample matrix which is usually achieved through gas diffusion [23,24] or pervaporation [16,25,26].

Recently, efforts have been focused on the miniaturizing of sample preparation, leading to the development of micro-extraction methodologies. One of effective extraction methods is single-drop micro-extraction. The single-drop liquid–liquid micro-extraction [27–29] and the liquid droplet [30–32] are successfully used for flow analysis of both liquids and gases, respectively. Headspace single-drop micro-extraction (SDME) [33] can be used for separation and concentration of volatile analytes in flow analysis, but this possibility has not been realized.

The aim of this work was to develop a new automatic stepwise injection headspace single-drop micro-extraction system (SWIA-HSDME) for volatile compounds determination in complicated matrices. The stepwise injection system is one of the universal solutions for the automation of analytical reactions in which the equilibration in the reaction is reached but dispersion of the reactants is prevented [34]. The SWIA-HSDME was successfully

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applied for determination of ammonia in concretes based on indophenol-blue reaction.

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical reagent grade. Ultra pure water from Millipore Milli-Q RG (Millipore, USA) was used for solution preparation and dilution.

The stock solution of ammonium ion was prepared by dissolving the corresponding amount of NH_4Cl in water. Working solutions of ammonium ion were prepared immediately before the experiments by dilution of the stock solution.

The 0.01 M solution of sodium salicylate was prepared immediately before the experiment by mixing 0.03 M solution of sodium salicylate, 3 mM solution of sodium nitroprusside and 0.03 M solution of sodium hydroxide in a ratio of 1:1:1 respectively. 1 mM solution of sodium hypochlorite was prepared immediately before the experiment by dilution of 0.1 M solution of sodium hypochlorite.

2.2. Manifold and apparatus

The SWIA-HSDME manifold (Fig. 1) includes: two solenoid valves (Cole-Parmer, USA), peristaltic pump Master Flex L/S (Cole-Parmer, USA) ensuring a reverse flow (flow rate is from 0.5 to 5 mL min^{-1}), syringe pump (Cavro XLP 6000, Tecan, USA), thermostated mixing chamber (MC) (a cylindrical-shaped glass tube with a funnel-shaped inlet at the bottom, 20 mm in height and 10 mm in i.d.), 50 mm path length flow cell FIA-Z-SMA-50-TEF (Fialab, USA), 2 mL polypropylene vial in a ultrasonic bath and communication tubes (PTFE, 0.5 mm in i.d.). An LS-1 tungsten lamp (Ocean Optics Inc., Dunedin, USA) was used as the light source, and a fiber-optic CCD USB 2000 (Ocean Optics Inc., Dunedin, USA) was used as the detector.

A Capel 103 RT capillary electrophoresis system equipped with a UV detector (Lumex, Saint-Petersburg, Russia) was used with an uncoated fused-silica capillary of 75 μm i.d., 50 cm effective length and 60 cm total length.

2.3. Sampling

Sampling from a concrete walls was carried out using a perforator (the depth of perforation was 1 cm). Then the concrete powder was placed in a polypropylene vial and sent to the laboratory.

2.4. SWIA-HSDME procedure

0.5 g of concrete sample was placed in a polypropylene vial (2 mL) and 1 mL of 0.1 M NaOH was added to convert of ammonium ions into volatile ammonia. The vial was capped immediately and mixed thoroughly. Steel needle (the length is 30 mm) connected to a syringe pump (SP) by the valve (V2) (Fig. 1) was inserted into the headspace of sample solution. Then 0.1 mL of the absorption solution (0.1 M H_3PO_4) was injected in the needle (port 8) by the SP and a microdrop of acceptor solution was suspended from the needle tip. After a certain period of time, the plunger was withdrawn and the microdrop was retracted back into the channel (port 9). In the next step the microdrop was delivered into the MC by an air stream where 0.1 mL of 0.01 M sodium salicylate (4) and 0.1 mL of 1 mM solution of sodium hypochlorite (3) were aspirated by the V1 and the peristaltic pump (PP). The air stream (port 1) was aspirated into the MC for solution mixing. Temperature control (40 °C) of the reaction mixture was carried out for 4 min to form indophenol-blue complex. At the final stage, the reaction mixture was moved from the MC into the flow cell of detector via the port 5 by the PP. The absorbance was measured under stop-flow conditions ($\lambda=660$ nm) for 20 s, after that the sample solution was delivered to the waste. To avoid the memory effects between samples the manifold was rinsed with deionized water.

2.5. Capillary electrophoresis procedure

1 g of the concrete sample was placed in a glass vial (10 mL) then 2 mL of water and 2 mL of 0.1 M solution of sodium hydroxide were added. Chromatographic syringe needle was punctured through the septum of vial and 5 μL microdrop of 0.1 M solution of phosphoric acid was generated. The vial was exposed to SDME with ultrasound for 10 min at 60 °C. After that the drop was retracted back into the syringe. The needle was removed from the headspace and its content was introduced to a vial for CE analysis (Russian GOST 53887-2010) with minor modifications.

Briefly, background electrolyte (BGE) contained 20 mM benzimidazole, 4 mM tartaric acid and 2 mM 18-crown-6. The capillary was rinsed for 5 min with 0.1 M sodium hydroxide solution and for 10 min with water and BGE at the beginning of each day. Between runs the capillary was rinsed with BGE for 3 min. The sample was filled up to 0.1 mL with water and injected into CE unit by a pressure of 0.5 psi. The injection time was 5 s. Separation was carried out at a constant voltage of 13 kV. Indirect UV detection was performed at 254 nm. All CE procedures were conducted at 20 °C.

3. Results and discussion

3.1. Optimization of parameters in the SWIA-HSDME manifold

3.1.1. Optimization of spectrophotometric determination

In order to find the optimal conditions for the ammonia determination by the indophenol-blue reaction, the influences of reagent concentrations, temperature and time were studied. For this purpose 0.1 mL of 3 mM NH_4^+ , 0.05 mL of solution of sodium salicylate (10–30 mM), 0.05 mL of solution of sodium nitroprusside (1–5 mM) and 0.1 mL of sodium hypochlorite solution (0.5–2 mM) were aspirated into the MC via the V1 by using PP (Fig. 1). Solutions were mixed in the MC by air stream (port 1), which was delivered at a rate of 5 mL min^{-1} for 1–10 min. The temperature in the MC was varied from 20 °C to 60 °C.

It was found that the optimal concentrations of sodium salicylate, sodium nitroprusside and sodium hypochlorite solutions were

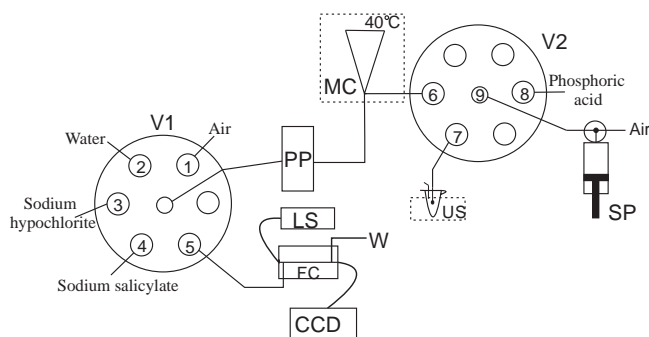


Fig. 1. The SWIA-HSDME manifold for determination of ammonia in concrete: V1 and V2 – valves, PP – peristaltic pump, LS – light source, CCD – detector, MC – mixing chamber, US – ultrasonic bath, SP – syringe pump, and W – waste.

20 mM, 2 mM and 1 mM, respectively. Raising the sodium salicylate and sodium nitroprusside concentrations does not lead to significant increases in absorbance, while increasing the sodium hypochlorite concentration leads to the destruction of the indophenol-blue complex. The maximum absorbance was observed at 40 °C for 4 min.

3.1.2. SWIA-HSDME performance

The possibility of SWIA-HSDME was studied to eliminate the interference of complicated matrices of concretes on the ammonia determination. The sample suspension should be alkaline enough ($\text{pH} > 10$) in order to convert NH_4^+ into volatile ammonia. A solution of phosphoric acid has a relatively high boiling point; it does not evaporate in the vapor phase during extraction and thus was selected as the acceptor solution.

To select the optimal concentration of NaOH and H_3PO_4 for the SWIA-HSDME, 0.5 mL of 1.7×10^{-5} M NH_4^+ and 1 mL NaOH (0.01–1 M) were placed in a vial, then the 5 μL microdrop of H_3PO_4 (0.01–1 M) was suspended by the SP. Headspace SDME of analyte was held in US bath for 10 min at 60 °C. Then the drop was analyzed by using indophenol-blue reaction. The optimal concentrations of NaOH and H_3PO_4 were equal (0.1 M). Further increase in concentrations of NaOH and H_3PO_4 does not lead to significant increase in absorbance.

To obtain reproducible results, it is necessary to mix the suspension of the sample. Three techniques of suspension mixing were studied: an ultrasonic mixing, a magnetic stirrer and air bubbles (the speed of 5 mL min^{-1}), wherein the temperature was changed from 20 °C to 80 °C. As the temperature increased above 60 °C the drop breakdown was observed in all cases due to condensation of water vapor on the needle. Ammonia emission in case of ultrasonic mixing at 60 °C is found to be the most efficient (Fig. 2). It should be noted that this technique is the most simple and allows us to vary the volume of suspension in a wide range.

The effect of a microdrop volume on the extraction completeness was studied. Generally, as the surface area increases with a drop volume expansion, the mass transfer from solution to the drop is expected to be more efficient. However, drops of more than 5 μL volume were unstable and fell out from the needle tip; therefore the maximum possible drop volume was selected as the optimal one.

The effect of the insertion depth of the steel needle into the vial was studied. It was found that varying the insertion depth did not affect the results of the experiment.

At the last optimization step of SWIA-HSDME conditions, the effect of mixing time in the US bath was examined. It has been found that 10 min is enough to complete the extraction (Fig. 3).

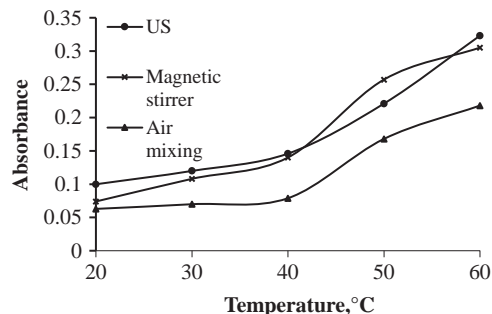


Fig. 2. The effects of the mixing technique on the ammonia emission (1.7×10^{-5} M NH_4^+ , mixing time is 10 min).

3.2. Interference effect

The impact of potentially interfering ions on the ammonia determination was investigated. It was performed by addition of known concentration of each ion to fixed NH_4^+ concentration. The tolerable concentration of each taken foreign ion is considered to be less than 5% of the relative error in the signal.

Mg^{2+} , Ca^{2+} , Fe^{3+} ions have significant influence on the indophenol-blue formation in 20-, 100-, and 100-fold excess, respectively (see Table 1). These ions are found in significant amount in concretes. However, the headspace SDME allows us to eliminate their influence completely.

The influences of volatile compounds (formaldehyde, triethylamine, and diethylamine), which may be present in concrete samples were not detected.

3.3. Analytical performance

For the generation of the calibration curve 0.1 mL of $0.5\text{--}5.0 \text{ mg L}^{-1}$ ammonium ion solution, 0.4 g of the calcined powdered concrete (ammonia content less than 0.1 mg kg^{-1}) and 1 mL

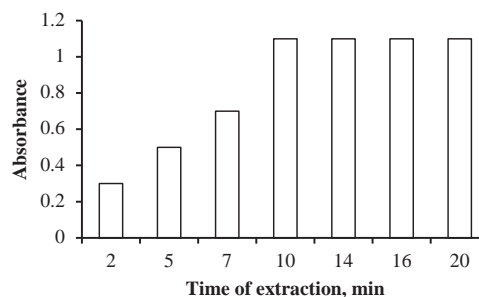


Fig. 3. The effect of extraction time on the ammonia emission (5.6×10^{-5} M NH_4^+ , US mixing, 60 °C).

Table 1

Influence of some interfering ions on the determination of ammonia (1 mM NH_4^+).

Species	Tolerable concentration (mM)
Ca^{2+}	7
SO_4^{2-}	> 100
NO_3^-	> 100
CO_3^{2-}	> 100
Mg^{2+}	1.4
F^-	> 100
Fe^{3+}	7
Formaldehyde	> 100
Triethylamine	> 100
Diethylamine	> 100

Table 2

Analytical performance data.

Parameter	SWIA-HSDME
Sample weight (g)	0.5
Drop volume (μL)	5
Time of HSDME (min)	10
Linear range (mg kg^{-1})	0.1–1
Correlation coefficient	0.9995
LOD (mg kg^{-1})	0.03
RSD ($n=5$) (%)	5
Time of analysis (min)	16

Table 3The results of ammonia determination in concretes ($n=5$, $t=2.776$, $P=0.95$).

Concretes	Found carbamides (mg kg ⁻¹)	Added NH ₃ (mg kg ⁻¹)	Found NH ₃ by SWIA-HSDME (mg kg ⁻¹)	Found NH ₃ by CE (mg kg ⁻¹)	$t_{\text{calculated}}$
1	60	0	0.53 ± 0.05	0.48 ± 0.04	1.966
		1	1.58 ± 0.07	1.50 ± 0.07	2.215
2	23	0	0.39 ± 0.03	0.38 ± 0.03	0.719
		1	1.36 ± 0.07	1.39 ± 0.07	0.823
3	382	0	1.10 ± 0.06	1.06 ± 0.05	1.384
		1	2.05 ± 0.08	2.11 ± 0.09	1.435

of 0.1 M NaOH were added to a 2 mL polypropylene vial, after which the SWIA-HSDME procedure was performed.

A calibration curve was obtained from eight data points over the range of 0.1–1 mg kg⁻¹ for ammonia. The LOD was calculated from the calibration plots based on 3 σ was 30 $\mu\text{g kg}^{-1}$. The precision was examined using RSD values: for two concentration levels (0.1 mg kg⁻¹ and 1 mg kg⁻¹). RSD values constitute 5% and 3%. Analytical performances of the technique developed are represented in Table 2.

3.4. Analytical application

The developed automated procedure was applied for the determination of ammonia in concrete walls of new buildings. Sampling was carried in premises where the ammonia content in the air exceeded the permissible daily average concentration of 0.04 mg m⁻³. Two samples of concrete were collected from each wall by perforation. Concrete powder samples were placed in vials and sent to the laboratory for analysis using the SWIA-HSDME and the CE as a reference method.

The significant contents of ammonia were found in all samples of concrete. Ammonia emission indoor is observed mainly due to hydrolysis of carbamides which are usually used as antifreeze additives in concrete mixtures in wintertime. Carbamides contents were also determined in concrete samples according to the method proposed in [35]. There is a correlation between a content of ammonia and carbamides in concretes (Table 3).

Analytical results obtained for the samples by the SWIA-HSDME and CE are presented in Table 3. The paired t -test shows that the ammonia contents found by the SWIA-HSDME method was insignificantly different from those obtained by CE method at a 95% confidence level.

4. Conclusions

The idea of automation of headspace single-drop micro-extraction has been implemented based on stepwise injection analysis. The most important features of the SWIA-HSDME are: automated determination of volatile compounds in complicated matrices including suspension; the successful coupling of the continuous operating process of headspace single-drop micro-extraction with the VIS/VIS technique. The efficiency of the proposed SWIA-HSDME system was successfully demonstrated in ammonia determination in concretes. The problem of significant influence of complex matrices was completely avoided by using SWIA-HSDME system. The suggested approach can also be applied to procedures

for the determination of other volatile analytes in different samples.

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