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# Stepwise injection spectrophotometric determination of carbamides in construction materials

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**Abstract**

A simple, convenient and express flow-based technique for the determination of carbamides in construction materials was developed. It is based on the reaction of Schiff bases formation by reacting carbamides with p-dimethylaminobenzaldehyde. The linear range was 20 to 400 mg/kg with LOD 6 mg/kg. The sample throughput was 23/h. This method has been successfully applied for carbamides determination in construction materials.

**Keywords** Stepwise injection analysis, carbamides, construction materials, p-dimethylaminobenzaldehyde

## 1. Introduction

The construction industry is one of the fastest growing and largest industries around the world. Concrete mixtures are widely used and produced on a large scale in the construction industry. Different additives which can contain carbamides are introduced into concrete mixtures to improve the technical characteristics. Furthermore, carbamides may be present in the cement used for preparation of concrete mixtures. However, as the temperature and humidity increase, these factors lead to increased indoor air pollution due to continuous transformation of carbamides into gaseous ammonia and emission into the indoor [1]. Residential and office spaces with high ammonia content are not suitable for life or work [2]. On the basis of this problem there is a need to control the content of carbamides in construction materials.

Fluorometric and photometric methods have found wide distribution for carbamides determination in different objects of analysis.

The reaction with diacetylmonoxime in acidic medium is proposed for the fluorimetric determination of carbamide [3, 4]. The product obtained exhibit two fluorescence maxima, at 410 and 525 nm. The main drawback of this method is a rapid reduction of the fluorescence intensity that is partially corrected by injection thiosemicarbazide and iron (III) in reaction [5], another disadvantage is the toxicity of the reagents used.

Photometric technique of carbamide determination has been proposed by the authors who uses the above-mentioned reaction of carbamide with diacetylmonoxime in acidic medium in the presence of iron chloride (III) and thiosemicarbazide [6, 7]. The technique has a high accuracy and reproducibility, but its use is complicated by the length of the analysis.

The enzyme techniques [8-13] are the most widespread in the clinical analysis suggesting the destruction of carbamide by the action of urease enzyme or leucine dehydrogenase followed by determination of ammonium ions.

The reaction of Schiff bases formation previously proposed for the determination of carbamide in biological fluids [14-19] can be used to determine carbamide in building materials.

Preliminary tests revealed that aqueous extracts of concrete samples taken from facilities excreting ammonia enter into a fast and sensitive reaction with Ehrlich's reagent (p-dimethylaminobenzaldehyde) to form a Schiff base colored.

This fact underlay the automated photometric method for determining carbamides in construction materials designed for rapid quality control in the mode of on-site. Stepwise Injection Analysis (SWIA) [20] was selected for automation since this method provides the widest possibility of solving the problems of the analysis automation without a loss in sensitivity due to dispersion as well as unification of the design of the hydraulic schemes[21].

## 2. Experimental

### 2.1. Manifold and apparatus

Absorption spectra and absorbances were measured using SHIMADZU UVmini-1240 (Shimadzu Scientific Instruments, Japan) spectrophotometers equipped with 10 mm light-path cell.

The flow system for the SWIA determination of carbamides (Fig.1) was based on flow analyzer SWIA-2 (Rosanalit, Saint-Petersburg, Russia). It included a bidirectional peristaltic pump ensuring a reverse flow, a six-port titanium valve, a reaction vessel (RV) which had cylindrical shape and was funnel-shaped at the bottom (glass tube 350 mm in height and 10 mm in i.d.), and communication tubes (PTFE, 0.5 mm in i.d.). It was equipped with a fibre-optic spectrophotometer USB 4000 (Ocean Optics Inc., USA) with flow cell of path length 50 mm (FIA-Z-SMA-50-TEF, FIALAB, USA) and a UV source (Model D 1000 CE, Analytical Instrument System Inc., USA).The analyzer was operated automatically by means of a computer.

Syringe 7.6 B002 (5 ml, Simas, Moscow, Russia) and syringe filter 7.5 B106 (Simas, Moscow, Russia) were used to filter extracts.

### 2.2. Reagents and solutions

All chemicals used were of analytical-reagent grade.

The stock carbamide solution was prepared by dissolving 0.1 g $CO(NH_2)_2$ in 100 ml of distilled water. The working solutions of carbamide were prepared immediately before the experiments by dilution of the stock solution.

The stock reagent solution was prepared by dissolving 1.00 g of p-dimethylaminobenzaldehyde in 5 ml of concentrated

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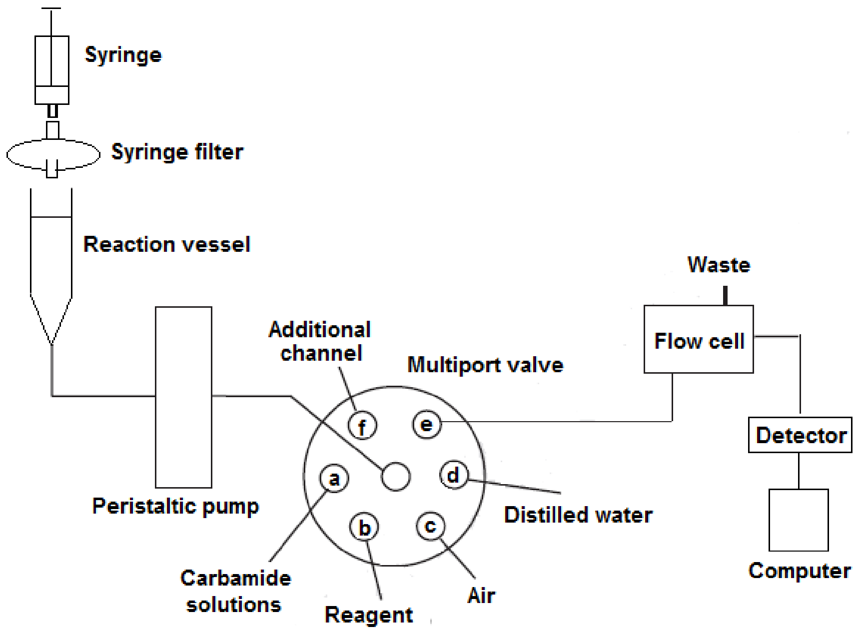



Fig. 1. The scheme of the manifold for the SWIA determination of carbamides.

hydrochloric acid and subsequent dilution with distilled water up to a volume of 50 ml.

Extractant was prepared by dissolving 0.5 g of ascorbic acid and 0.05 g of sodium sulfite to stabilize acid in 100 ml of distilled water.

2.3. Sampling and sample preparation

To determine carbamides in building materials the samples of 10 to 20 g were taken from the mixer at the construction site. The sample was shaken with 10 ml of extractant for 1 min. After sedimentation of the suspension the aqueous extract was moved in a 5 ml syringe. Then 0.2 ml of the filtrate was squeezed by the rod of syringe through the syringe filter into reaction vessel of SWIA.

2.4. Procedure for the determination of carbamides performed in the SWIA mode

According to the scheme of SWIA (Fig. 1) 0.2 ml of a 20 g/l solution of p-dimethylaminobenzaldehyde (b) was supplied through the multiport valve with reversible pump into the reaction vessel with 0.2 ml of the filtrate and then the air is supplied through the channel (c) within 20 s at a rate of 5 ml/min for mixing solutions. After that the solution of Schiff base was sent from the RV to the fiber flow cell spectrophotometric detector and its absorbance was measured in the mode of «flow stop».

At the final stage a flush of the communications system was performed. For that 0.4 ml of distilled water was supplied through the channel (d) in the RV, which then was sent through the cell of the detector to waster.

## 3. Results and discussion

3.1. The wavelength selection

At the preliminary stage the absorption spectra of the reaction products of p-dimethylaminobenzaldehyde with different nitrogen-containing organic compounds (amines, carbamide) and water extracts of the concrete buildings with ammonia emission were taken. The peaks in absorption spectra for all the reaction products of these substances with a colour-forming reagent are observed in the range from 400 to 440 nm. For further research wavelength 415 nm was chosen because the absorption maxima for the reaction products of p-dimethylaminobenzaldehyde with carbamides from concrete samples are observed at this wavelength.

Maxima in the absorption spectra for the reaction products of the colour-forming reagent with carbamide and concrete extracts are the same, therefore for further research it was used the aqueous carbamide solutions at choosing the optimal conditions. And all concentrations of analytes were converted to the content of carbamide.

3.2. The optimal concentration of p-dimethylaminobenzaldehyde and the acidity

To select the optimal concentration of the colour-forming reagent 0.2 ml of 100 mg/l carbamide solution (a) and 0.2 ml of 20 g/l p-dimethylaminobenzaldehyde (b) were fed into the RV (Fig. 1). The concentrations of colour-forming reagent were varied from 2.5 to 30 g/l.

The optimal concentration of the solution of p-dimethylaminobenzaldehyde was chosen to be 20 mg/l (Fig.2).

To optimize the conditions for carbamides determination the pH influence on the efficiency of flow colour-forming reaction was examined in the range from 1 to 10. The results presented (Fig. 3) shows that the absorbance is almost unchanged in the pH range 1-4 and at pH more than 4 it is observed the decreasing of absorbance of the reaction product. For further experiments pH 1 was selected providing a complete colour-forming reaction and also eliminating the possibility of colloidal solutions formation at analyzing of aqueous extracts of concrete mixtures.

3.3. The effect of extractants and the extraction time

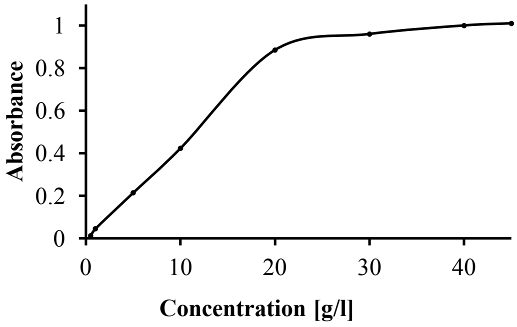



Fig. 2. Influence of the absorbance of the reaction products of carbamide solution (100 mg/l) with different concentrations of p-dimethylaminobenzaldehyde solution.

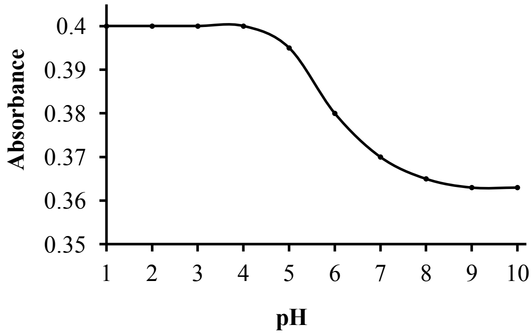



Fig. 3. Influence of the absorbance of the reaction products of carbamide (50 mg/l) with p-dimethylaminobenzaldehyde (20 g/l) on pH of the solution.

Distilled water and solutions of hydrochloric acid with different concentrations 0.1, 0.5, and 1 mol/l were studied as extractants. It was established that the efficiency of carbamides extractions from concrete mixtures into these extractants was the same. Therefore, distilled water was selected for further research. It should be noted that the muddy colloidal solutions may be obtained after filtration of aqueous extracts; however, a true solution is formed by the addition of hydrochloric acid reagent solution.

Also the influence of extraction time of carbamides from the concrete mixtures on the absorbance was investigated. It can be concluded from the data (Fig. 4) that the optimum extraction time of carbamides is one minute.

3.4. The study of the time mixing and the temperature

The analytical signal in SWIA depends on the mixing time of the solutions in the reaction vessel. For mixing 0.2 ml of 100 mg/l carbamide solution and 0.2 mL of 20 g/l p-dimethylaminobenzaldehyde solution the airstream was fed in the reaction vessel at a rate of 5 ml/min herewith the temperature was maintained at 20 $^0$C in it. The optimal mixing time for carbamide solutions (curve 1) and aqueous extracts of concrete (curve 2) is sown in Fig. 5. It is 20 seconds.

The influence of the temperature at the rate of occurrence of the colour-forming reaction in the RV was studied additionally. It was established that the temperature in the range of 20 to 60 ° C does not affect the formation of the reaction products.

3.5. The study of the interference

The effects of different compounds belonging to the construction materials (cement, concrete mixtures) on carbamide determination with p-dimethylaminobenzaldehyde were studied. For this purpose interference species in the range of $10^{-5}$ to 2 mol/l were introduced into $2\cdot10^{-3}$ mol/l solution of carbamide. No interference was found when including up to 1000-fold $Ca^{2+}$, $K^+$, $Na^+$, $Fe^{2+}$, $Al^{3+}$, $NO_3^-$, $SO_4^{2-}$. However, there are influences of sulphites, nitrites, Cr (VI) and Fe (III) in Table 1. It should be mentioned that sulfites have a reducing property and nitrites, Cr (VI) and Fe (III) being present in the sample increase the analytical signal on the contrary. To eliminate interference such serious interfering ion as Fe (III), Cr (VI) and $NO_2^-$ it is necessary to introduce ascorbic acid in the extractant. Ascorbic acid reduces the interference species abovementioned to Fe (II), Cr (III) and $NO_3^-$, which do not interfere in carbamides determination.

Table 1. Influence of some ions on the carbamide determination

| Species | Interferes with concentration, mol/l |
|---|---|
| $Fe^{3+}$ | $10^{-3}$ |
| $Cr^{6+}$ | $10^{-4}$ |
| $SO_3^{2-}$ | $1.2\times10^{-2}$ |
| $NO_2^-$ | $1.4\times10^{-4}$ |

3.6. Calibration curve

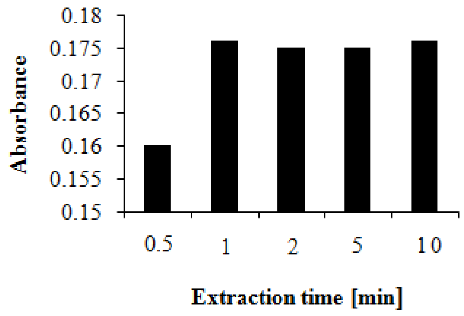
To build a calibration curve stock carbamide solution was fed instead of filtrate to the RV through the channel a (Fig. 1). Under optimal conditions the linear detection range obtained was from 20 to 400 mg/kg carbamide (correlation coefficient 0.9995), with a detection limit of 6 mg/kg and precision characterized by an R.S.D. 3% for n=3. The sample throughput was found to be 23/h.

3.7. Sample analysis

The technique developed was tested on real objects from different building facilities in St. Petersburg during different seasons. Samples were taken from concrete mixers and transferred for analysis in a mobile laboratory equipped with SWIA. The correctness of the technique developed has been confirmed by experiments by the add-found method. The tendency of carbamides content to decrease in concrete from the winter to the summer period is seen in Table 2. This is due to antifreeze additives which are introduced into the concrete during the winter.

Table 2. The results of carbamides determination in concrete mixtures (n = 3, P = 0.95)

| Sample | Added, mg/kg | Found, mg/kg | Recovery, % |
|---|---|---|---|
| Concrete 1 | 0 | 382 | |
| (winter) | 50 | 428 | 98 |
| Concrete 2 | 0 | 60 | |
| (spring) | 50 | 112 | 102 |
| Concrete 3 | 0 | 23 | |
| (summer) | 50 | 72 | 96 |



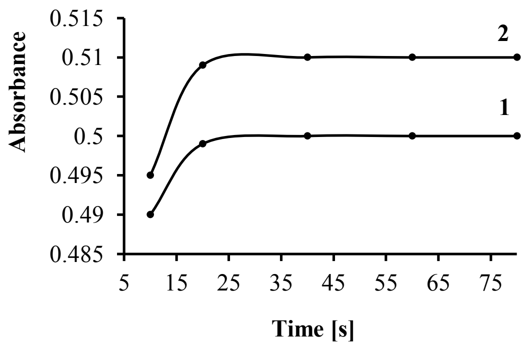




Fig. 4. Influence of the absorbance of the solution of the analytical form on carbamides extraction time from the concrete mixture (sample weight of 20 g).

Fig. 5. Influence of the absorbance of the reaction products of carbamide solution (the concentration of 125 mg/l) (curve 1) and concrete extract (the concentration of carbamide is 130 mg/kg) (curve 2) on mixing in the RV.

## 4. Conclusion

The technique which includes the pre-extraction of carbamides from construction materials to the aqueous phase and subsequent determination by the method of SWIA based on colour-forming reaction with p-dimethylaminobenzaldehyde was developed. The method has been successfully applied for the determination of carbamides in construction materials. Analytical performances of the technique developed are presented in Table 3.

Table 3. Analytical performances of the technique developed

| Parameter | SWIA method |
|---|---|
| Volume of sample (ml) | 0.2 |
| Volume of p- dimethylaminobenzaldehyde (ml) | 0.2 |
| Time of stirring with air in reaction vessel (s) | 20 |
| Linear range (mg/kg) | 20 - 400 |
| Correlation coefficient | 0.9995 |
| LOD ( mg/kg) | 6 |
| R.S.D % | 3 |
| Sampling throughput (per hour) | 23 |

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