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## DETERMINATION OF NITROGEN IN WATER TECHNOLOGY

### STANOVENÍ DUSÍKU V TECHNOLOGII VODY

#### Abstract

By the survey presented in this paper the methods used for determining nitrogen in water technology are described. There are the several nitrogen forms which are important for water treatment and must be routinely analysed: ammonia, nitrates, nitrites, and total and organic nitrogen. The list of analytical procedures is not complete and it is focused at the most frequently used methods. The paper is intended to inform, in short, technologists and/or other people responsible for water treatment technology about the up-to-date analytical procedures and their application. Preferably, the standardized methods are mentioned.

#### Abstrakt

V příspěvku je uveden přehled analytických metod, které se používají v technologii vody ke stanovení dusíkatých sloučenin. Jejich výčet není úplný a omezuje se na nejčastěji používané postupy pro stanovení těch forem dusíku, které jsou z hlediska technologických procesů důležité: amoniakální dusík, dusičnany, dusitany, celkový a organický dusík. Článek si klade za cíl informovat technology a ostatní pracovníky o současných postupech a jejich principech. Přednostně jsou uvedeny metody, které jsou normalizované.

**Key words:** determination, nitrogen, ammonium, nitrites, nitrates, water.

#### Introduction

The majority of nitrogen occurrence in waters comes from rainfalls and rinses of agriculture soil. A small part of nitrogen originates from sewage and industry wastes. Nitrogen plays an extraordinary role in all biological processes taking place in the surface, ground and waste waters. There are several forms of nitrogen naturally existing in the environment: gaseous nitrogen, ammonia nitrogen, nitrates, nitrites and many organic compounds which are simply classified as organic nitrogen.

The amount of nitrogen in treated waters is controlled by an appropriate technology. The limit concentrations of nitrogen in drinking waters are strictly given by the regulation [1] because of their toxicity for human organism. In waste/cleaned waters the limits of nitrogen are also restricted by, e.g. by [2] to avoid the eutrofisation of surface water.

There is a lot of analytical methods that can be utilized for quantification of nitrogen in water: volumetric analysis, spectrometry, potentiometry, electrophoresis, liquid chromatography, polarography etc. Only some of them are routinely used in water technology. The standardized procedures are applied preferably because they are fully validated and internationally accepted. The aim of this article is to give a brief account of the methods used for the determination of inorganic and organic nitrogen species in water with respect to the treatment technology.

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## Determination of ammonia nitrogen

Ammonia nitrogen in water comprises of dissociated ammonium and gaseous ammonia. The ratio of both forms depends on pH and the temperature of water. Ammonium is mostly determined by the spectrometric method based on its reaction with salicylate and hypochlorite. This reaction produces blue coloured compounds of indophenolic type [3] of which absorbance is measured at 655 nm. The detection limits are reported in the range of 0,003 to 0,008 mg/l. By comparing to the limit 0,5 mg/l for drinking water [1] it is obvious that the indophenolic method is applicable for the analysis of raw and tap water as well. This method has replaced the former Nessler procedure that was based on the reaction of ammonium with mercury tetraiodide. The Nessler method was less selective and sensitive, and it also gave the false positive results. By looking at the results of the ring test organised in the Czech Republic in 2001, it is very striking that 18 out of 84 laboratories have still used this procedure.

In wastewater and/or sewage, ammonium is often determined by the potentiometric method [4] using the ionic selective electrode (ISE). The analysed samples are alkalined firstly and then the released ammonia is measured by the membrane ISE. Because of easy handling, the specially adapted electrodes are often installed at exit of water works for continual monitoring of ammonium in effluents.

The high concentrations of ammonium in wastewater are determined by the distillation and titration method [5] as well. The distillation of ammonia is also recommended for sample preparation of the spectrometric method in order to eliminate the disturbance of water matrix. Distilling ammonia is entrapped into the solution of boric acid and titrated by hydrochloric acid using bromothymol blue as the indicator. Boric acid is recommended to be replaced by sulphuric acid because of carbon dioxide which is absorbed together with ammonia and titrated as well. Besides this effect, the method tends to provide the false positive results due to presence of other compounds distilled together with ammonia and react with the volumetric solution: e.g. urea, volatile amines etc.

In case of a great number of samples (up to 100 per an hour), the continues injection (CIA) and flow injection analysis (FIA) are used. Ammonia is separated by diffusion through a semi-permeable membrane and spectrometrically determined [6] after its reaction with the mixed pH indicator.

The isotachophoretic analysis of ammonium in ground, surface and drinking water was described in the standard [7] as well. Ammonium is separated at the same time with other ions such as sodium, potassium, calcium and magnesium. The separation takes about 10 minutes.

The samples for the determination of ammonia nitrogen, which cannot be analysed immediately after sampling, must be preserved by sulphuric acid at  $\text{pH} < 2$  and stored at temperature 2 to 5 °C for max. 24 hours [8]. Before the analysis the samples are usually prepared by filtration (centrifugation) and/or by distillation if necessary. Paper filters are not suitable because they release ammonium during filtration.

## Determination of nitrates

Nitrates occur in all types of waters. In drinking water, their concentration must not exceed 50 mg/l for adults and 15 mg/l for babies. Nitrates are mainly determined by the spectrometric methods.

In these methods, nitrates work as nitrification agents that react with various aromatic compounds producing coloured derivatives. The standardized methods are based on the reaction of nitric acid with 2,6-dimethylphenol [9], 4-fluorophenol [10], and sulfosalicylic acid [11]. None of them is universal. The method with 2,6-dimethylphenol is rapid and easy to use but not suitable for waste and saline waters. Chlorides cause higher results and therefore they must be removed by e.g. precipitation with  $\text{AgNO}_3$ . In case of the reaction with 4-fluorophenol, the product 2-nitro-4-fluorophenol is distilled from the reaction mixture. This procedure is very laborious and time consuming, but selective and applicable for all types of waters. In addition, it is possible to work with the irritant (4-fluorophenol) and highly flammable compounds (toluene).

The most wide-spread method is based on the reaction of nitrates with sulfosalicylic acid. The approached detection limits of  $\text{N-NO}_3^-$  are referred to be 0,003 to 0,013 mg/l if 40 mm measuring cells are applied. We have already described the modified procedure [12] which is easier for the sample manipulation. Besides the interfering compounds obtained in the procedure [11], it is very important to alkaline the solution before evaporation to avoid losses of  $\text{HNO}_3$ .

Nitrates can be also determined after their reduction into ammonium or nitrites. The reduction can be done with Devarda's alloy [13] into ammonium and with cadmium amalgam or hydrazinium sulfate [13] into nitrites. The reduction with cadmium is used for the purpose of the CIA and FIA [14].

In addition to the above described spectrometric methods, nitrates can be also analysed directly in the UV-spectrum by the measuring of absorbance at 210-220 nm [15]. The procedure is quick and simple but an influence of nitrites, carbonates, organic compounds,  $\text{Cr}^{\text{VI}}$ , and  $\text{Fe}^{\text{III}}$  were found. It is possible to remove carbonates by acidification of samples. Other interfering effects can be minimized by a correction based on the measuring of absorbance at two wavelengths. Organic compounds can be removed by adding active carbon. This determination is recommended only for the analysis of drinking and/or clean waters. For this type of samples the potentiometric analysis with ISE is recommended as well [13]. The nitrate electrode is based on a liquid membrane consisting of crystal violet dissolved in nitrobenzene.

In order to complete the list of standardized methods, liquid chromatography of ions [16, 17] and capillary isotachopheresis [18] for determination of nitrates and nitrites should be mentioned. The main advantage of these separation methods is the determination of several ions in one analytical run with minimal disturbing effects of other ions. Unlike liquid chromatography, utilization of capillary isotachopheresis is confined to low contaminated waters.

The samples are stored and preserved as in case of ammonia nitrogen. Preparation before analysis can be carried out by filtration (centrifugation) or dilution. The coloured samples can be clarified by adding active carbon or aluminium hydroxide.

### **Determination of nitrites**

The presence of nitrites in waters is most critical for ground and drinking waters where it indicates fresh faecal pollution. Concentrations up to 0,5 mg/l in tap water are allowed [1]. The mostly utilized spectrometric methods are based on the ability of nitrites to diazotize aromatic amino compounds producing diazonium salts which are copulated to create azo-dye. The most frequently diazotized aromatics are sulphanilic acid and/or its amids. Consequently, these diazonium salts are let to react with 4-(1-naphtyl)-ethylene-diamine dihydrochloride [19] that replaced the former 1-naphtylamine which was found to be carcinogenic. The absorbance of the coloured substances is measured at 540 nm. The detection limits are declared to be about 0,002 mg/l.

The samples could be stored at temperature 2 to 5 °C for max. 24 hours [8]. The sample preparation is similar to the one in the case of nitrates.

### **Determination of organic nitrogen**

Organic nitrogen  $\text{N}^{\text{III}}$  occurs in surface and waste waters and/or is produced by the chemical and food industry. Organic nitrogen is bonded in proteins, lipids, amino acids, urea and is presented in nucleosides. This parameter, as total and inorganic nitrogen (see below), belongs to the category of so the called group parameters which give only a sum of all related compounds. The knowledge of organic nitrogen is important for controlling the biological treatment of waste waters.

The determination of organic nitrogen is based on the transformation of  $\text{N}^{\text{III}}$  into ammonium. This analytical procedure has been developed by Kjeldahl in 1883 and is still used in various modifications. The samples are decomposed by concentrated sulphuric acid in the presence of a catalyst. Before this procedure, ammonia must be removed from samples by distillation. After mineralization, the solution is alkalined and the produced ammonia is separated by distillation and consequently determined by one of the appropriate methods for ammonium determination. There are several digestion methods that differ in the application of catalysts. It has been proved that the most useful catalyst is mercury [20] and its mixture with selenium [21]. Because of its high toxicity, mercury has been replacing by selenium nowadays [22]. Instead of this tedious procedure, organic nitrogen is used to be calculated as the difference of total nitrogen and the sum of inorganic nitrogen forms, i.e. mostly ammonium, nitrates and nitrites.

The concept of Kjeldahl's nitrogen is also known in water treatment practice. It stands for the sum of organic and ammonia nitrogen. The quantification of this parameter is described in the standard [22]. The samples are decomposed by Kjeldahl's procedure without a preliminary removal of ammonia. Ammonium is then quantified after digestion.

### **Determination of total nitrogen**

Total nitrogen consists of inorganic and organic nitrogen. There are three principal procedures of how to decompose all nitrogen species and transfer them into a single type of measurable compounds: Kjeldahl's digestion, Koroleff's digestion by oxidation with peroxodisulfate and ignition of samples.

The first approach is based on the reduction of nitrate and nitrite into ammonium followed by Kjeldahl's digestion of samples. The reduction can be carried out directly by Devarda's alloy [23] or by zinc [21] after reaction with phloroglucinol. Phloroglucinol forms nitro- and nitrosophloroglucinol which are reduced by zinc into their amino derivatives. The mineralized samples are alkalined and ammonia is distilled and determined.

Under the second approach, the alkalined water samples are digested by oxidation with peroxodisulfate at about 150 °C and increased pressure conditions [24]. The samples can be heated in a microwave oven or in an electric heating block. Nitrates, produced by the digestion, are determined by conventional methods.

By using the third procedure [25], the nitrogen compounds are catalytically ignited in the oxygen atmosphere at 1000 °C forming NO that reacts with ozone as follows:



Chemiluminescent lighting in the range of 700 to 900 nm of the excited molecule  $\text{NO}_2^*$  is detected. The analyzer is sometimes equipped with devices for determination of total organic carbon in water as well. The nitrogen compounds could also be oxidized into  $\text{NO}_x$  and measured by infrared spectrometry, or reduced into  $\text{NH}_3$  and determined by spectrometry or microcoulometry. These procedures are not typical for the plant laboratories and they are mentioned here as an example of another possibility of quantification of the total nitrogen.

The samples for the determination of both organic and total nitrogen can be preserved by sulphuric acid at  $\text{pH} < 2$  and stored at temperature 2 to 5 °C for max. 24 hours [8].

### **Determination of inorganic nitrogen**

Inorganic nitrogen is analysed because of requirements regarding the quality of effluents from sewerage and wastewater treatment plants to river water [2]. This parameter is supposed to be the sum of nitrate, nitrite and ammonium. This suggestion does not have to hold for industrial outlets containing the other inorganic nitrogen compounds, such as cyanides and thiocyanides from coal carbonisation.

Another approach is the calculation of the difference between total nitrogen and organic nitrogen. This procedure is more time consuming because of tedious Kjeldahl's mineralization.

### **Laboratory result transmission**

A very important issue, which is also worth mentioning, is the way of transmission of laboratory results to technologists and other responsible workers within a company as fast as possible. Daily sending of the results as paper forms or test reports is very time consuming and problematical because of the data storage and treatment. The most effective way proved by the plant laboratory is the use of the Laboratory Information and Management Systems (LIMS) [26] within the company's computer network. Certain employees outside of the laboratory have an access to the laboratory database under these conditions at any time. However, they can only retrieve and statistically evaluate the data without the possibility of modifying them. In addition, they are not authorised to look at the results of external clients.

During our practice with LIMS, we have found its application of automatic generation of alert e-mails which are sent to the workers in charge very useful. LIMS creates these warning messages as soon as the results, having been entered into the database by laboratory workers, do not comply with the given limits. It enables the company to make corrective interventions in technology in a short time.

## Conclusion

For the running of water works it is necessary to know the composition of water during all the important technological steps. Water processing comprises of treatment and delivery of drinking water, as well as carrying away and cleaning of wastewater. The relevant nitrogen parameters are ammonium, nitrite, nitrate, and total and organic nitrogen.

Suitable analytical methods must be sufficiently precise, accurate, and quick to obtain correct information about the treatment processes in time. The selection of the appropriate analytical procedure also strongly depends on the concentration of analytes as well as on water contamination. In addition, the used methods have to be selected with respect to their economy and risk of laboratory wastes.

Plant laboratories usually choose the easy handling and quite robust volumetric and spectrometric methods: Ammonium is mostly determined by the spectrometric method with salicylate and hypochlorite, by the ionic selective electrode and by titration with hydrochloric acid. Nitrates are analysed by the methods based on the reaction of nitric acid with 2,6-dimethylphenol, 4-fluorophenol and sulfosalicylic acid. Nitrites are quantified by the spectrometric methods based on their ability create diazonium salts which react with N(1-naphthyl)ethylenediamine dihydrochloride. The determination of organic nitrogen is based on the transformation of  $N^{III}$  into ammonium according to Kjeldahl. Total nitrogen is determined as ammonium after the digestion according to Kjeldahl, as nitrates after oxidation with peroxodisulfate and by catalytical ignition in the oxygen atmosphere at about 1000 °C forming nitrogen oxides.

The analytical methods, developed in a laboratory, must be fully validated. Accuracy and sufficient precision of the laboratory results can be ensured by the good working quality system which is desired to be certified by accreditation [27].

A very effective way of laboratory result transfer within company is the use of LIMS. Selected employees outside of a laboratory are able to retrieve the results in the laboratory database through the company computer network. Their access is checked by passwords and it is confined only on data-viewing, without possibility of their modification. The ability of having the information in real time is very important for the decision-making process.

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## Resumé

Stanovení dusíku patří mezi základní požadavky kladené na vodohospodářské laboratoře. Koncentrace dusíku se sledují v jednotlivých fázích technologie výroby a transportu pitných vod a při čištění a stokování odpadních vod. Sledují se hodnoty dusičnanů, dusitanů, amonných iontů, celkového a organického dusíku. Na vyústěních kanalizační sítě do povrchových vod se dle vyhlášky č. 47/1999 Sb. [2] sledují i koncentrace anorganického dusíku, kterým se rozumí suma dusičnanů, dusitanů a amonných iontů.

Stanovení těchto parametrů zajišťují provozní laboratoře vodárenských společností. Pro analýzu jednotlivých dusíkatých látek existují řady metod, z nichž jsou nejčastěji voleny metody normalizované nebo plně validované, pokud jsou vyvinuty v laboratoři. Jejich výběr závisí na požadované přesnosti a koncentračním rozsahu analytu. Dále je nutné přihlížet k rizikovosti vznikajícího odpadu, ekonomické náročnosti a rychlosti jednotlivých metod. Z těchto důvodů se v provozních laboratořích nejčastěji volí metody titrační nebo spektrometrické: Při stanovení amonných iontů se podle typu vod volí titrace kyselinou chlorovodíkovou, iontově selektivní elektroda nebo spektrofotometrická metoda se salicylanem. Pro stanovení dusičnanů se používají fotometrické metody založené na schopnosti dusičnanů v kyselém prostředí nitrovat 2,6-dimethylfenol, 4-fluorfenol a kyselinu sulfosalicylovou. Dusitany se stanovují rovněž fotometricky na základě vzniku azobarviva s N-(1-naftyl)-ethylen-diamin dihydrochloridem. Celkový a organický dusík se stanovují po mineralizaci na amonné ionty metodou podle Kjeldahla nebo jako dusičnany po oxidační mineralizaci s peroxidisíranem podle Koroleffa.

V dnešní době je již samozřejmý systém vnitřní a vnější kontroly jakosti, např. formou akreditace laboratoře [27], který zajišťuje správnost a dostatečnou přesnost analytických výsledků.

Úkolem laboratoří není jen provádět potřebné analýzy, ale i efektivně předávat výsledky pracovníkům v provozech. K tomuto účelu velmi dobře slouží laboratorní informační a manažerský systém [26] používaný v rámci podnikové počítačové sítě. Tento systém je určen pro činnost laboratoří, ale mohou jej sdílet i ostatní vybraní zaměstnanci k zobrazování či statistickému zpracování výsledků rozborů. Přístup je chráněn hesly a omezen právy, které uděluje správce systému. Rychlý přenos dat k uživatelům umožňuje účinně zasahovat při technologických závadách.

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