

SPECTROPHOTOMETRIC DETERMINATION OF SODIUM AZIDE IN WORKPLACE AIR

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ABSTRACT

Sodium azide (NaN_3) is a colourless or a white crystalline powder, odorless, with hexagonal crystal structure. Sodium azide is used in detonators and other explosives in military industry, in agriculture (farming) for pest control, as a chemical preservative in hospitals and laboratories and as the chemical in automobile airbags. Sodium azide is a source for production of lead azide and other heavy metal azides, used as detonators. In workplace air sodium azide may be found like disintegrated aerosol. Sodium azide is extremely toxic. The workers are exposed to sodium azide principally by inhalation and by skin. The methods described in the literature concern determination of sodium azide in air and in various biological samples. Some of them satisfy the hygiene requirement for monitoring of sodium azide in workplace air, but it is not provided for technical resources anywhere in Bulgarian chemical laboratories at this time. In this paper the fully validated spectrophotometric method is described for determination of sodium azide in workplace air, which is suitable for frequent application in the hygiene practice. Air sampling at workplace air is made by means of perchlorovinyl filters (FPP). Water extraction for 30 minutes from FPP-filters is used. A simple spectrometric procedure with hydrochloric acid and iron (III) salts is described. The average recovery is $89.4 \pm 14.7\%$. The method has a wide linear range: from 0.01 to 1.0 mg cm^{-3} at the wavelength of maximal absorption ($460 \pm 2 \text{ nm}$). Observation limit is 0.003 mg cm^{-3} . Determination limit is 0.008 mg cm^{-3} . The uncertainty in sodium azide measurement by described spectrophotometric method was estimated by Kragten-GUM mode [16] and its value is 21.88% . The method is simple and rapid. It has suitable sensitivity to determine sodium azide levels in workplace air in accordance with threshold limits and requires the widely-spread popular equipment as well as personal training is not necessary.

Keywords: sodium azide, spectrophotometry, workplace air.

INTRODUCTION

Sodium azide (NaN_3) is a colourless or a white crystalline powder, odourless, with hexagonal crystal structure and easily soluble in water. Its specific gravity is 1.84 and melting point 275°C .

The azide ion is the part, which is responsible for much of molecules' reactivity. The azide group is made up of three nitrogen atoms joined together. This is a very unstable arrangement and consequently the azide will readily react to gain the more stable configuration of nitrogen gas. This is the driving force of the

explosive reactions of sodium azide. At heat, shock or friction sodium azide explodes strongly.

Sodium azide is used in detonators and other explosives in military industry, in agriculture (farming) for pest control, as a chemical preservative in hospitals and laboratories. It is well known as the chemical found in the automobile airbags. Sodium azide is a source for production of lead azide and other heavy metal azides used as detonators.

The leading role for occupationally exposed workers to sodium azide is to examine chemical factors, particularly at the workplace, where sodium azide

is dosed or used. It is known that in workplace air sodium azide may be found as a disintegrated aerosol. The workers are exposed to sodium azide principally by inhalation and by skin. Sodium azide is extremely toxic and is, in fact, as powerful as a poison as sodium cyanide and ingesting very small amounts can cause death in less than half an hour. Potential symptoms resulting sodium azide exposure are: irritation of eyes, skin, headache, dizziness, nausea, vomiting, diarrhea, weakness, temporary loss of vision; low blood pressure, fainting; palpitation, tachycardia; kidney changes; decreased plasma creatinine; nasal stuffiness; cough, shortness of breath; trembling of the hands. At doses up to 10 mg/kg: convulsions, coma pulmonary edema, shock, metabolic acidosis, arrhythmia, bradycardia, asystole are described in literature [1, 2]. In reports since 2004 it seems that red blood cells, perhaps via the enzyme *catalase*, can convert azide to nitric oxide, a potent vasodilator. [3, 15]. Ingestion or aspiration of sodium azide may be fatal. In order to characterize the known health effects of sodium azide in humans and the circumstances of their exposure S. Chang and S. Lamm conducted a systematic review of the literature from 1927 to 2002 on human exposure to sodium azide and its health effects [4]. The authors reported that the most commonly health effect from azide exposure is hypotension, and the most industrial exposures are by inhalation.

Health Legislation sets the next Exposure Limits for sodium azide in workplace air: 0.3 mg m⁻³ by Occupational Safety & Health Administration (OSHA) [5] and 0.29 mg m⁻³ [6] by American Conference of Government Industrial Hygienists (ACGIH). In Bulgarian Legislation there was not a Limit Value (LV) for sodium azide in workplace air until 2005. Ordinance Number 13 of the Ministry of Labor and the Social Policy and the Ministry of Health for workers' protection against risks related to exposure to chemical agents at work (30 December 2005) sets the LV for sodium azide into the workplace air: time-weighted average (TWA) for 8 hours - 0.1 mg m⁻³ and for 15 min - 0.3 mg m⁻³ [7]. Because the chemical factors are of particular significance for the occupational risk assessment and the Exposure Limits are available in Bulgarian Legislation, a method for determination of sodium azide concentrations in the workplace air has been developed.

Various methods for sampling, sample preparation and determination of sodium azide are described for the purpose of exposure assessment in workplace air

[8-12]. In general most of them have not a suitable sensitivity at short-term sampling needed to meet threshold limits. Some of these methods are subject to interferences from many compounds (for example nitrites, bromides, adipic acid). Frequently it is difficult to adapt the sampling to the analytical method. The OSHA Salt Lake Technical Center previously used a stopgap method for sodium azide [13]. Samples were collected with impingers, which were inconvenient to use as personal samplers due to possible spillage of the liquid collection solutions or breakage [14]. It was attractive to develop a solid-sorbent sampling and analytical method capable of measuring sodium azide in accordance with threshold limits requirements. Such one was evaluated using a base-impregnated silica gel (ISG) as the collection media [12].

At present time OSHA recommends a method as following: The sampling is made by means of PVC filter or in the glass wool plug of the sampling tube. Gaseous HN₃ is collected and converted to NaN₃ by the ISG sorbent within the sampling tube. The collected azide on either media is unstable at buffer solution. The resultant azide anion N₃⁻ is analyzed by IC with UV detection at 210 nm. A gravimetric conversion is used to calculate the amount of sodium azide or hydrazoic acid collected [13, 14]. The methods described in the literature concern determination of sodium azide in air and in various biological samples. The IC-method recommended by OSHA, satisfies the hygiene requirement for monitoring of sodium azide in workplace air, but it is not provided for technical resources anywhere in Bulgarian chemical laboratories at this time. In this paper the fully validated spectrometric method is described for determination of sodium azide in workplace air, which is suitable for frequent application in hygiene practice. It is simple and rapid. It has the suitable sensitivity to determine sodium azide levels in workplace air in accordance with threshold limits. At last, this method requires the widely-spread popular equipment and personal training is not necessary.

EXPERIMENTAL

Reagents

All chemicals and reagents were extra pure. They are purchased from Merck. The sodium azide stock solution was prepared by dissolving 300 mg sodium azide (extra pure) in 100 cm³ distilled water. The hydrochloric acid solution (1:3) is prepared by addition of 50 cm³ hydro-

Table 1. Performance data of the spectral method for determination of sodium azide in air.

No.	Standard Concentrations (mg.cm ⁻³)	Number of samples	Average absorption (n = 10)	Average concentration, calculated by standard equation, (mg.cm ⁻³)	Standard deviation	Coefficient of variation, (%)
	Blank	30	0.0019	-	0.0011	57.80
1.	0.01	10	0.0204	0.014	0.0044	21.81
2.	0.02	10	0.0392	0.028	0.0045	7.68
3.	0.05	10	0.0612	0.046	0.0038	6.19
4.	0.1	10	0.1178	0.089	0.0050	4.27
5.	0.3	10	0.3854	0.294	0.0058	1.50
6.	0.5	10	0.6702	0.505	0.0068	1.01
7.	0.7	10	0.9430	0.711	0.0068	0.72
8.	1.0	10	1.3166	0.993	0.0085	0.65

chloric acid (extra pure, 37 %) to 150 cm³ distilled water. The iron (III) chloride solution is prepared by dissolving 16.6 g FeCl₃·6H₂O (pure) in 100 cm³ distilled water.

Equipment

All analyses are performed on UV/VIS spectrophotometer Perkin-Elmer "Lambda-5". The standard laboratory glassware was used.

Sampling

Based on the physical and chemical properties of sodium azide and because it is known that sodium azide can be found in air at the workplace as a disintegrated aerosol, the sampling from workplace atmosphere was developed. The suitable method is the air aspiration from workplace atmosphere at 2 to 20 dm³.min⁻¹ through the FPP-15 perchlorovinyl filters. There are available the FPP-15 filters with d 48 mm for stationary sampling and d 37 mm for personally sampling. Both types of pumps (personal and stationer) are widely used in occupational measurements. The pump used is calibrated at working rate of air aspiration. The precision of sampling time measurement is ± 0.1 min. The air volume is estimated like air at standard conditions (20°C, 1013 h Pa) by formula:

$$V_0 = \frac{V_t \times 293 \times P}{(273 + t) \times 1013}$$

where V_0 is the volume adjusted to standard conditions, $t(C)$ is the sampling temperature, V_t is the volume at the sampling conditions and P is the sampling pressure.

Sample preparation

The FPP-filters were extracted with 4 cm³ distilled water for 30 min at a room temperature. The 3 cm³ of each water extract was transferred to a volumetric flask of 10 cm³ for the next analyses. At the same time a series

of standard solutions of sodium azide was prepared in a range of 0.01 to 1.0 mg cm⁻³ by diluting the stock solution. The standard solutions and the FPP-extracts are developed at once. To each of them were consecutively added 1 cm³ hydrochloric acid (1:3) and 1 cm³ 10 % iron (III) chloride solution. The content in flask was mixed better whenever the reagent was added. The intensity of yellow colour of the end product of reaction was corresponding to the sodium azide concentration.

Spectrophotometric procedure

UV/VIS spectrophotometer Perkin-Elmer "Lambda-5" was used. The wavelength of maximal absorption (460 ± 2 nm) was determined experimentally by scanning of a series of sodium azide standard solutions (from 0.1 to 1.0 mg cm⁻³).

The calibration graph *absorption/concentration of sodium azide* was linear. It is described by the equation:

$$Y = 1.3248 \cdot X + 0.0006$$

where Y is absorption at concentration X and correlation coefficient is 0.9993. The limit of observation is 0.003 mg cm⁻³. The limit of detection is 0.008 mg cm⁻³. Performance data obtained by the spectrophotometric method are presented in Table 1. The measurements are performed between 10th and 20th minutes since the end of spectrometric reaction.

This measurement is not selective, because the presence of sulfides, sulfates, thiosulfates and thiocyanates increased the absorption. Nitrates, usually presented in the processes of sodium azide production and use, do not hamper the spectral determination.

Recovery

Recovery of the method for determination of sodium azide in air was obtained using gravimetrically loaded FPP-filters. Air (500 cm³) was aspirated through

Table 2. Recovery of sodium azide by the spectral method with hydrochloric acid and iron (III) salts.

No	Amount (g), added gravimetrically to the filters	Quantity (g), determined by spectrometric method	Recovery, %
Blank ₁	0	0.000097	-
Blank ₂	0	0.000073	-
Blank ₃	0	0.000089	-
Blank ₄	0	0.000113	-
1.	0.0018	0.0018	100.0
2.	0.0012	0.0011	91.6
3.	0.0010	0.0012	120.0
4.	0.0015	0.0013	86.7
5.	0.0030	0.0022	73.3
6.	0.0020	0.0020	100.0
7.	0.0010	0.0008	80.0
8.	0.0010	0.0009	90.0
9.	0.0018	0.0016	88.9
10.	0.0026	0.0023	88.5
11.	0.0007	0.0005	71.4
12.	0.0017	0.0014	82.4

the loaded filters and they were extracted with distilled water (4 cm³). The 3 cm³ of water extract obtained was analyzed by spectrometric method with hydrochloric acid and iron (III) salt and the results obtained are presented in Table 2. The recovery obtained for 0.0007-0.0030 g sodium azide per filter was 89.4 ± 14.7 %. This result satisfies the requirement for the determination of sodium azide in workplace air for hygiene purposes. The uncertainty in sodium azide measurement by the described spectral method was estimated by Kragten-GUM mode [16] and its value is 21.88 % mainly given by the extraction from FPP-filter (56.7 %).

DISCUSSION

The developed spectral method is suitable for the determination of time-weighted average (TWA) for 8 hours concentration of sodium azide in workplace air. For this purpose it is sufficient to aspirate through filter about 400 dm³ of air. The method permits to determine 30 % of short-time limit value for estimation of 15 min exposure if to aspire air with rate of 20 dm³.min⁻¹ for all 15 min. This method is simpler than that described in the literature and is sufficiently precise for the application to the monitoring of concentration in workplace air with sodium azide aerosols during production and use. The general disadvantage is that it is unselective in the presence of sulfides, sulfates, thiosulfates and thiocyanates.

REFERENCES

1. A.Kleinhofs, W.M. Owais, R.A. Nilan: Azide. Mutat. Res., 55, 1978, 165-195.
2. R.P Pohanish, Hydrazoic acid, Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens, Fourth Ed., v.1. Norwich, NY: Noyes Publications, William Andrew Publishing, 2002, 1269-1270.
3. M. Shahidullah, Role of catalyze in the smooth muscle relaxant actions of sodium azide and cyanamide Eur. J. Pharmacol., 435, 1, 2002, 93-101.
4. Soju Chang, S. Lamm, Human Health Effects of Sodium Azide Exposure: A Literature Review and Analysis, Int. J. of Toxicology, 22, 3, 2003, 175-186.
5. http://www.osha.gov/dts/chemicalsampling/data/CH_267505.html
6. http://www.ehs.neu.edu/hazardous_waste/fact_sheets/sodium_azide/
7. Ordinance No13 of Ministry of Labor and Social Policy and Ministry of Health (30 December 2003) for workers' protection against risk related to exposure to chemical agents at work, DV/8, (30 January 2004), validity since 2005.
8. L.C. Westwood, E.L. Stockes, Determination of Azide in Environmental Samples by Ion Chromatography. Ion Chromatographic Analysis of Environmental Pollutants, v. 2, edited by J.J. Mulick and E. Sawicki. Ann Arbor, MI. Ann Arbor Science, 1979, 141.
9. C.E. Roberson, C.M. Austin: Colorimetric Estimation of Milligram Quantities of Inorganic Azides Anal. Chem. 29, 1957, 854-855.
10. K.E.Williams, G.G. Esposito, D.S. Rinehart, Sampling Tubes for the Collection of Selected Acid Vapors in Air, Am. Ind. Hyg. Assoc. J. 42, 1981, 476-478.
11. J.M. Zehner, R.A. Simonaitis: Gas Chromatographic Determination of Hydrazoic Acid., J. Chromatogr. Sci., 14, 1976, 493-494.
12. M.A.Puskar, S.M. Fergon, L.H. Hecker, A Short-Term Solid Sorbent Determination of Hydrazoic Acid in Air., Am. Ind. Hyg. Assoc. J., 52, 1, 1991, 14-19.
13. Occupational Safety and Health Administration Salt Lake Technical Center: Azide by Ion Chromatography (Stopgap Method - Unpublished) by J. Germ, Salt Lake City, UT, 1985.
14. OSHA Sodium azide and Hydrazoic Acid in Workplace Atmospheres, ID-211 <http://www.osha.gov/dts/sltc/methods/inorganic/id211/id211.html>
15. Safety and Health Topics: Sodium Azide, http://www.osha.gov/dts/chemicalsampling/data/CH_267505.html
16. GUM-Guide to Expression of Uncertainty in Measurement, ISO, 1995.