PHOTOMETRIC DETERMINATION OF MICROGRAMME QUANTITIES OF 1,3,5-TRINITRO-1,3,5-TRIAZACYCLOHEXANE IN AIR

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Received April 11th, 1983

A method is suggested for the determination of 1,3,5-trinitro-1,3,5-triazacyclohexane in workroom atmosphere. The substance is trapped in a sampling tube containing glass microfibres and activated silica gel, decomposed with sulphuric acid to give formaldehyde, the latter is reacted with 1,8-dihydroxynaphthalene-3,6-disulphonic acid, and the the derivative of dibenzoxanthilium-tetrasulphonic acid formed is determined photometrically at 580 nm.

Workers in the explosives industry are exposed to the hazard of inhalation of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX, hexogen), a substance irritating the central nervous system and causing tonicoclonic spasms similar to epileptic convulsions[1]. The highest admissible concentrations of hexogen in workroom atmosphere are relatively low; for instance, 1·0 mg m^{-3} in Poland and in the USSR and 1·5 mg . . m^{-3} in the USA (refs[2-4]). Environmental monitoring of this substance thus imposes stringent demands on the sensitivity of the analytical method employed as well as on the effectiveness of the prior sample collection. Having too high detection limits, methods[5-7] based on the basic hydrolysis of hexogen and the consecutive measurement of the intensity of the pink colour arising on the addition of Fe^{2+} are unsuitable for this purpose.

The objective of the present work was to develop and test a method for the determination of hexogen, meeting the demands of environmental monitoring. From this point of view, a route *via* formaldehyde appeared to be the most suitable. The method suggested is rapid and simple, and is sufficiently selective also with respect to 2,4,6-trinitrotoluene, a compound frequently accompanying the substance in question.

EXPERIMENTAL

Chemicals and Apparatus

Solution of 1,3,5-trinitro-1,3,5-triazacyclohexane (c = 45·0 mmol l^{-1}) in sulphuric acid was prepared by dissolving 250 mg of substance in 25 ml of concentrated H_2SO_4, and solution of 1,8-dihydroxynaphthalene-3,6-disulphonic acid was obtained by dissolving 500 mg of substance in 25 ml of distilled water. All the chemicals used were of reagent grade purity (Lachema, Brno).

Air sampling was accomplished by means of an MP 1 membrane pump (Chemoprojekt, Satalice) in conjunction with a PL 1 liquid gasometer (Východočeské plynárny, Skuteč).

Photometric measurements were performed on a VSU-2G instrument (Carl Zeiss, Jena).

Sample Collection

The substance was trapped from air aspirated through borosilicate glass tubes 120 mm long, *i.d.* 6 mm, packed with a 10 mm long filter insert of Akuver glass microfibres and an 80 mm long adsorbing layer of activated silica gel[8]. Prior to the assembling, the glass filter insert was washed with sulphuric acid and distilled water and dried at 150°C. The air flow rate was 500 ml min^{-1}, sampling period 100 min.

After the collection, the tube contents were transferred into a 25 ml volumetric flask containing 5 ml of sulphuric acid. After 20 min, 0·2 ml of dihydroxynaphthalenedisulphonic acid solution and 3·5 ml of distilled water were added, the flask was closed, and the contents were stirred thoroughly and allowed to cool down. The solution then was diluted to volume with water, and the intensity of the red-violet colour was measured at 480 nm in 5 cm cells against a blank solution.

RESULTS AND DISCUSSION

Based on the dependence of the hexogen vapour pressure on temperature[9,10], the relation $\log c + \log T = 20{\cdot}722 - 5\,576{\cdot}8T^{-1}$ has been derived[10]; here c is the equilibrium concentration of hexogen in air (μg m^{-3}) and T is the absolute temperature (K). Thus, at ambient temperature (17–23°C) the concentration of hexogen in vapours will be about 10^{-1} μg m^{-3}, which is negligible as compared with the highest admissible concentration values. So the dominant factor affecting the final result of analysis is the effectiveness of trapping aerosol particles by the filter element. The only suitable material available for this purpose, exhibiting a high collecting efficiency, is glass microfibres[10].

In the photometric measurements carried out with a standard solution of analyte in sulphuric acid, Beer's law was obeyed over the concentration region of 2 to 100 μg of hexogen in 25 ml sample. Eighteen duplicate measurements were performed to derive the regression straight line equation $A = ac + b$ (A is the absorbance, c, concentration in μg per 25 ml of solution) with the coefficients $a = 0{\cdot}0119 \pm 0{\cdot}009$, $b = 0{\cdot}0153 \pm 0{\cdot}0013$ (the confidence intervals apply to the 0·05 confidence level; the standard deviation characterizing the scatter about the regression straight line was $1{\cdot}55 \,.\, 10^{-2}$).

The slope ratio for equal concentrations of hexogen and formaldehyde respectively, $q = 1{\cdot}05 \pm 0{\cdot}11$, gives evidence that one molecule of 1,3,5-trinitro-1,3,5-triazacyclohexane is transformed into one molecule of formaldehyde under the conditions applied. It is clear from Fig. 1 that the optimum concentrations of sulphuric acid, most suitable for the formation of formaldehyde, are above 14 mol l^{-1}.

The data of Table I show that the interfering effect of trinitrotoluene in the determination of hexogen in low indeed: up to the trinitrotoluene-to-hexogen concentration ratio of 10 : 1 the error is negligible, and up to the ratio of 30 : 1 the error is tolerable with respect to the permitted error of determination of the pollutants in workroom atmosphere[11].

The method was tested by using samples prepared in a special evaporating apparatus[8]. With hexogen amounts of 50 ± 0·5 μg delivered into the tube tested, the relative standard deviation of determination, for a set of 8 samples, was s_r = 12·4%.

TABLE I

Effect of 2,4,6-trinitrotoluene on the results of determination of 1,3,5-trinitro-1,3,5-triazacyclohexane (hexogen)

Trinitrotoluene added μg	Hexogen added μg	Hexogen found μg	Relative standard deviation (n = 8) %
0	10	10·1	0·3
50	10	9·7	0·3
100	10	9·4	0·5
1 000	100	97·8	1·7
2 000	100	96·0	2·3
3 000	100	93·2	3·4

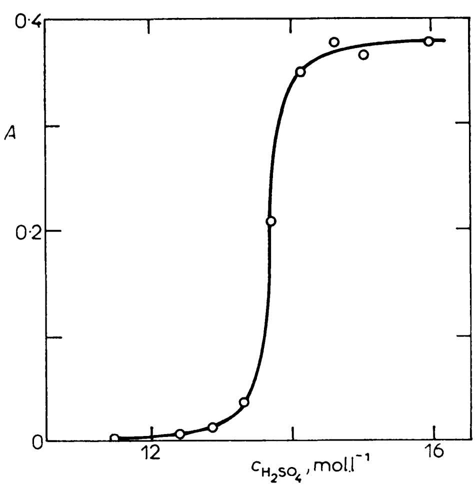

FIG. 1

Amounts of formaldehyde formed from 1,3,5-trinitro-1,3,5-triazacyclohexane in dependence on the concentration of sulphuric acid

The method is applicable to practically all technological operations in industrial use; all substances affording formaldehyde when reacted with sulphuric acid, however, interfere.

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Translated by P. Adámek.