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COLORIMETRIC METHOD FOR SEMIQUANTITATIVE DETERMINATION OF NITROORGANICS IN WATER

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Very low concentrations of TNT, 2,4-DNT, HMX and RDX were determined in water. Dissolved explosives were concentrated from very diluted aqueous solutions by means of isothermal equilibrium adsorption on an adsorbent of a limited surface area which was, by a special process, given the form of a porous film. Using visualization reagents (o-tolidine and Griess reagent) visibly coloured surfaces were obtained which, by direct colorimetric measurements in diffusely reflected light, using a referent curve, can be applied for determination of unknown concentrations.

KEY WORDS: Nitroorganics, equilibrium adsorption, reflected light colorimetry.

To satisfy permitted requirements, the daily monitoring of wastewater from explosive manufacture is necessary. This monitoring requires separate determination of TNT (2,4,6-trinitrotoluene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), the two most common explosives. Additionally, monitoring of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), also an often used explosive and a common impurity in RDX, and DNT (2,4-dinitrotoluene), a low-level impurity in TNT, may be required in the near future. At present no standard analytical method is available for the determination of TNT, RDX or HMX. Hence, a number of methods for explosive determination have been developed, but they differ widely in detection limits, specificity and precision.

Methods that have been used to determine these explosives in water include thin-layer chromatography,¹ gas-liquid chromatography,²⁻⁴ (reversed-phase) high-performance liquid chromatography,⁵⁻⁷ conversion to nitrate⁸ and colorimetry.⁹⁻¹¹

This work was undertaken to develop a suitable and simple method which must have detection limits sufficiently low to satisfy monitoring requirements and which should be inexpensive to implement. The main idea was to combine the isothermal equilibrium adsorption method¹² for sample preconcentration on an adsorbent surface. By photometric measurement of the visibly coloured surfaces of the adsorbent, and using a reference curve obtained by the same procedure, it is possible to determine the unknown concentration.

The basic characteristics of this method are: (i) establishment of the adsorption equilibrium under dynamic adsorption conditions on an adsorbent layer with a

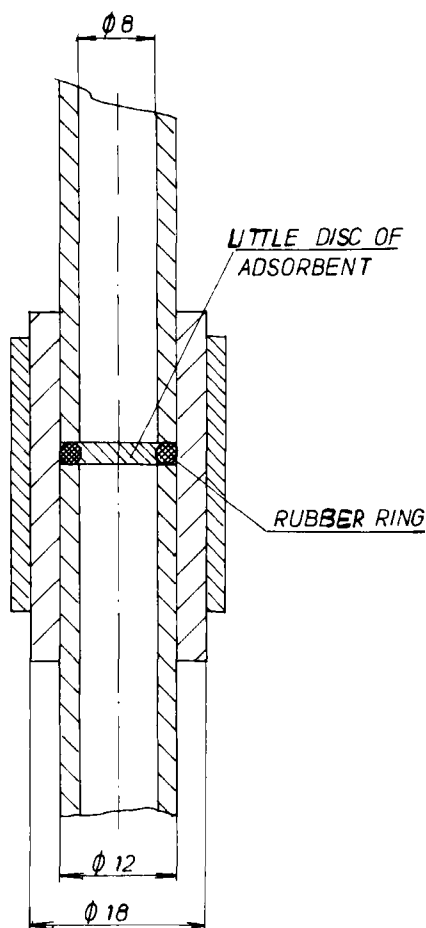


Figure 1 The adsorption column.

limited surface area and thickness, obtained by a special procedure; (ii) direct colorimetric measurement of the coloured surface of the adsorbent in diffusely reflected light.

EXPERIMENTAL

Apparatus

All adsorption experiments were conducted in an adsorption column, a long (1 m) and comparatively thin (diameter 8 mm) glass tube. The porous disc of adsorbent film was attached at the lower end of the column, as is shown in Figure 1. The adsorbent film could be well tightened by means of a piece of rubber tubing. Colorimetric measurements were conducted on a colorimeter constructed specially

for this purpose.¹⁵ The arrangements for colorimetric measurement, as well as the complete measurement procedure were described earlier.¹²

Materials

Silica gel HF 254 (Type 60, "Merck") was used as an adsorbent. The porous discs of silica gel were prepared by the following procedure: 15 cm³ of acetone and then 1 cm³ of 10% cellulose acetate solution were added to 0.5 g of previously dried powdered silica. The filter paper for quantitative filtrations was inserted into this suspension for 20 sec. After drying, the complex obtained—i.e. adsorbent film plus filter paper—was cut into discs 12 mm in diameter.

Standard Solutions

Stock standard solutions of TNT, DNT, and RDX were prepared by weighing 0.5 g of the solid material and dilution to 1 dm³ with distilled water. The saturated stock standard solutions thus obtained contain 130 mg/dm³ of TNT,¹⁶ 200 mg/dm³ of DNT¹⁷ and 50 mg/dm³ of RDX.¹⁶

The stock standard solution of HMX was prepared by weighing about 0.4 g of solid material and diluting it to 1 dm³ with 100% acetic acid. The concentration of this saturated solution was 370 mg/dm³ (ref. 17).

Standard solutions of explosives were prepared by diluting the stock standard solution 10–10000-fold.

Reagents

o-Tolidine reagent was prepared by dissolving 5 g o-tolidine in 250 cm³ 95% ethanol.

Griess reagent was prepared by mixing equal volumes of the following solutions before use: Solution 1 was prepared by dissolving 0.5 g sulfaminic acid in 50 cm³ acetic acid and 100 cm³ water and filtered. Solution 2 was prepared by dissolving 0.1 g α -naphthylamine in 120 cm³ boiling water. After cooling, 30 cm³ acetic acid were added and the solution was filtered.

Sodium hydroxide (1 mol/dm³) was prepared by dissolving 4 g NaOH in 100 cm³ water.

Procedure

In the course of the experiments 50 cm³ of a solution was passed through the adsorbent. A period of about one hour was necessary for this volume of solution to flow through the adsorbent. It was necessary to pass the same solution through the adsorbent twice, but to be on the safe side, three runs were made which, on the basis of the good reproducibility observed, should be considered quite sufficient in all cases.

Each dilution was analyzed in triplicate in order to check the reproducibility of

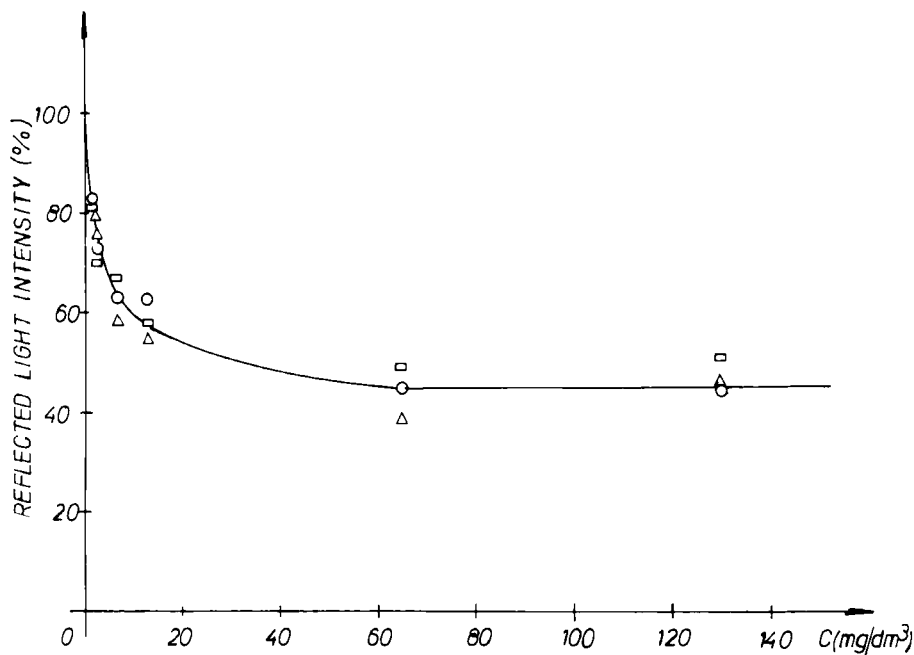


Figure 2 The intensity of coloration for three series of discs of silica in dependence of the initial concentration of TNT in water.

the results. Ten adsorption columns were in operation simultaneously. The flow rate of the solution was identical in all columns.

The adsorption being completed, the adsorbent was taken out of the column, and dried in the air, avoiding direct sunlight. The adsorbent discs were sprayed with the proper visualisation reagents according to common TLC methods¹³ and determined colorimetrically in diffusely reflected light. The blank was prepared by the same procedure using the same volume of distilled water. In order to reduce the non-homogeneity of the coloration ethanol was added in amounts of 5 cm³–50 cm³ to each analysed solution at a time, as a capillary active material.¹²

RESULTS AND DISCUSSION

The results of the measurements were represented by plotting the reflected light intensity (in per cent) vs. the corresponding solution concentration (in mg/dm³). A typical diagram for standard solutions of TNT is shown in Figure 2. In Figure 3 a series of discs of silica with visualised TNT adsorbent on them is shown.

In Figure 4 the results from Figure 2 are depicted on a semi-logarithmic scale. An almost straight line is obtained now. The reproducibility of the method is seen to be rather satisfactory.

In order to check the coloration homogeneity, special measurements were

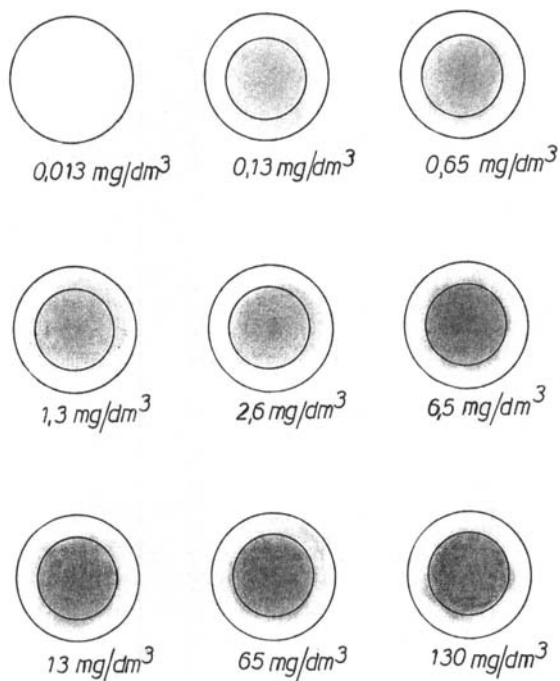


Figure 3 A series of little discs of silica with adsorbed TNT after visualization with o-tolidine.

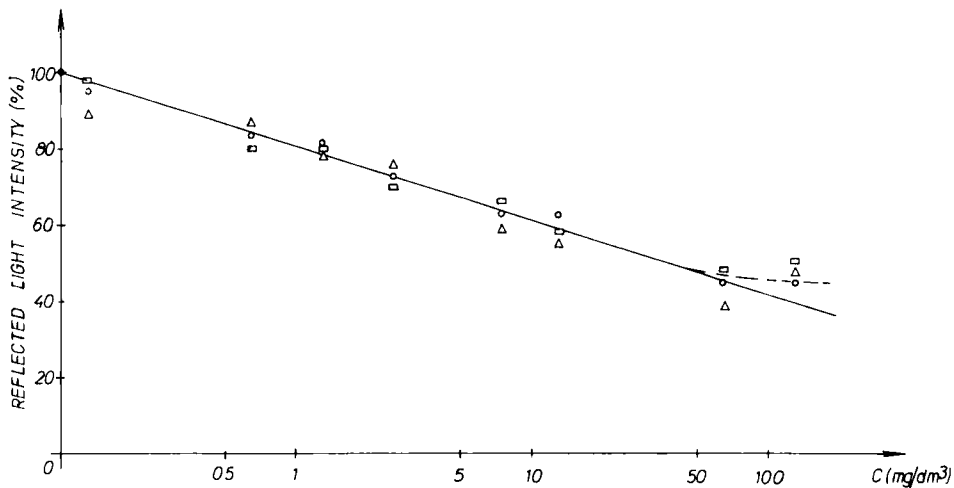


Figure 4 The intensity of coloration for three series of discs of silica as a function of the initial TNT concentration, plotted on semi-logarithmic scale.

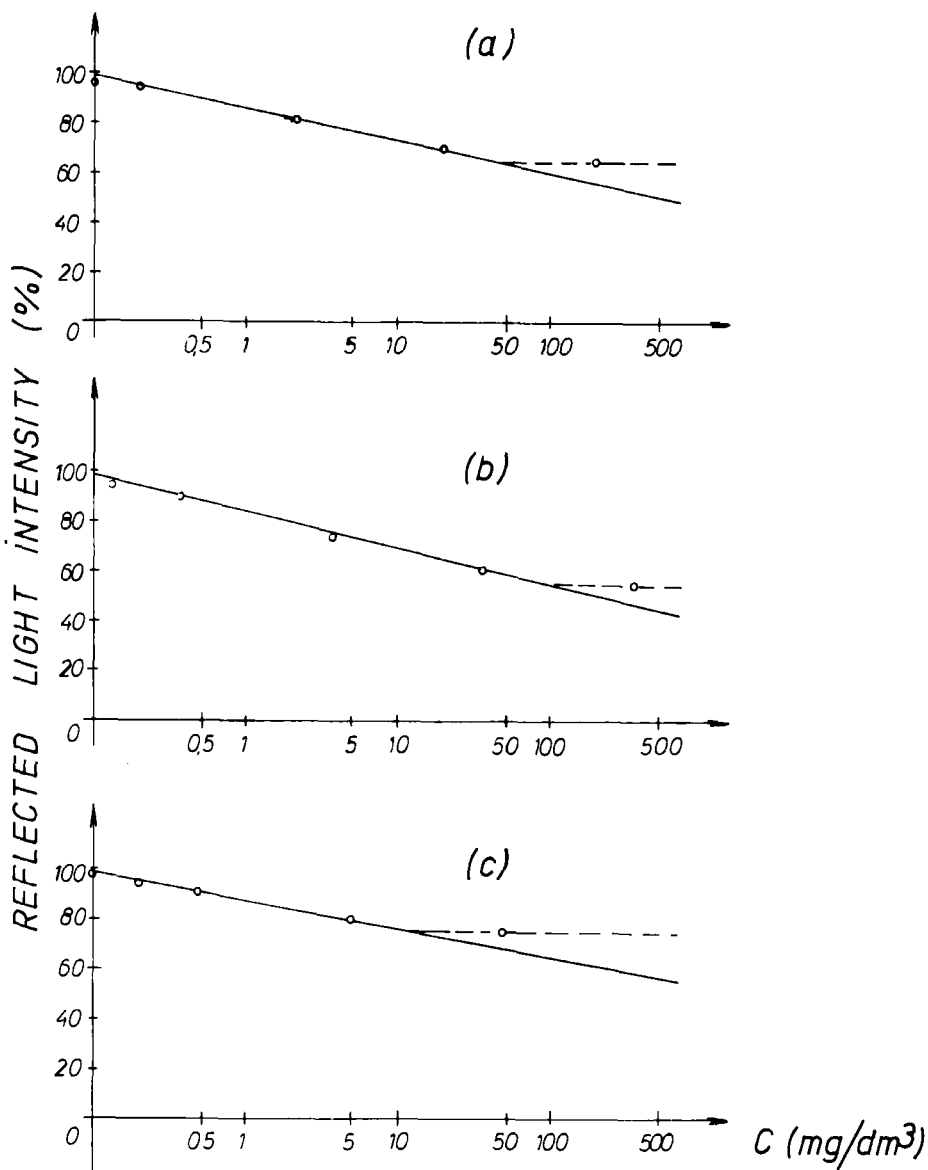


Figure 5 The intensity of coloration of discs of silica in dependence on the initial (a) HMX, (b) RDX and (c) DNT concentration.

carried out with statistically selected coloured discs of silica. Light intensity reflected from different points of the coloured surface was measured. The intensity of coloration appear to differ less than 10% from point to point over the whole coloured surface.

Results obtained when working with standard solution of DNT, HMX and RDX are presented in Figure 5. In all cases the data show a similar behaviour.

The data points corresponding with the lowest concentrations generally are slightly below the curve, which means that the spots are more intensely coloured than they should be. This can be explained by the fact that impurities (dust, colour from the rubber) have a relatively large influence. The results for extremely high concentrations, such as saturated solutions, are higher than expected which can be explained by saturation of the adsorbent. Therefore, reliable results will be obtained if working with different volumes of solutions for different ranges of explosive concentrations, i.e. greater volumes (500 cm³) for the concentrations of up to 1 mg/dm³ and smaller volumes (10 cm³) for concentrations of over 50 mg/dm³.

Detection limits are estimated at about 0.2 mg/dm³ in all cases, if the volumes of the explosive solutions are 50 cm³. Possibly the detection limits can be decreased by using larger working volumes of the solutions.

CONCLUSION

On the basis of the present results, one can conclude that the method may be useful for the semiquantitative measurement of dilute explosive solutions. As the quantity of solutes adsorbed is a function of analyte concentration only, unknowns may be determined rapidly using a previously constructed semi-logarithmic working curve. The reproducibility of the method appears to be satisfactory.

The method requires relatively large volumes for analysis and a relatively long working time. On the other hand, it is very simple and inexpensive and a number of adsorption columns can therefore be used at the same time. Because no reference method was available, the next step in the development of the method will be an interlaboratory test of this procedure.

The method, as developed so far, has certain disadvantages, it being unable to separate and determine various explosives in their mixtures, particularly RDX and HMX, since the same visualisation reagent is used for their determination. The next step in the development of this method will be to develop a procedure for separation of the explosives on the basis of TLC and adsorption chromatographic methods. The development of a standard technique for adsorbent discs preparation will be studied thereafter.

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