# An Automated System for Analysis of Nitro-Compounds in Water

by THOMAS L. HESS, LARRY J. GUIDRY, and STEVE D. SIBLEY
*US Army Environmental Hygiene Agency*
*Environmental Chemistry Division*
*Aberdeen Proving Ground, Md. 21010*

Trinitrotoluene and related compounds are contaminants in waste waters from munitions plants operations. Thus, there is need for a reliable and sensitive method for their detection at low concentrations (ppm) in water. It is further desirable to simultaneously determine other nitro or nitrate compounds present in same sample. A procedure has been developed that will allow such an analysis at low concentrations in an automated fashion. The method has been applied for the analysis of binary mixtures of explosives to obtain a separate analysis for both components.

## Procedure for Analysis

A two channel colorimetric analysis method is found to be most easily used for the problem. One channel reacts only with nitroaromatic compounds containing at least three ring substituted nitro groups. Trinitrotoluene (TNT), trinitrobenzene (TNB) and similar compounds will react to form a MEISENHEIMER (1902) complex under the action of a strong base. The second channel reacts with all other contaminants capable of forming nitrite ion which then is determined using a modified SALTZMAN (1954) diazo-complex reaction. A diagram of the experimental set-up is shown in the FIGURE.

A Technicon Instruments AutoAnalyzer I® is employed, with a 50 mm flow cell in each colorimeter channel, at a rate of 40 samples per hour. 15% KOH solution (3.67 M) was used in Channel I for alkaline hydrolysis of organic nitro groups prior to reaction with a modified SALTZMAN (1954) reagent (15 g tartaric acid, 1.5 g sulfanilamide, 0.05 g 2-naphthol-3,6-disulfonic acid disodium salt and 0.05 g N-(-naphthyl)-ethylenediamine dihydrochloride made to one liter of aqueous solution) that is acidified just prior to use with concentrated orthophosphoric acid (9 parts reagent to 1 part acid). Use of 0.58 M HCL solution for a wash reagent between samples eliminates color carryover. Use of a Teflon® probe in place of the normal metal one on the automatic sampler corrected an erratic baseline found with an acid wash. The colored complex formed was monitored at a wavelength of 550 nm and compared to an analytical calibration curve prepared from solutions of pure compounds. The second reaction in Channel II simply reacts the water sample with 15% KOH solution to produce a

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TABLE

Reagent Consumption Rate for Automated Analysis

| Substance | Channel I | Channel II |
|---|---|---|
| Sample | 2.00 ml/min | 1.60 ml/min |
| Air | 0.42 | 0.60 |
| KOH | 0.23 | 0.16 |
| Saltzman Reagent | 0.80 | -- |

Meisenheimer complex whose intensity can be monitored at 440 nm using an analytical calibration curve established from known solutions of the trinitroaromatic compound under study. The TABLE shows typical rates pumped through each channel.

## Application of Method to Samples

The determination of nitrocompounds in Channel I was found to be quantitative for both organic and inorganic substances. Thus, any source of nitrate or nitrite ions would act as an interference in the determination of mixed explosives, such as TNT and RDX (cyclotrimethylenetrinitramine). The response in this reaction is attributable to the total of all nitrocompounds present. Different compounds exhibit different levels of sensitivity and thus require separate calibration curves.

The determination of trinitroaromatic compounds in Channel II was found sensitive to 1 ppm of TNT. No detectable interference was found to occur from mono- or di-nitro-aromatic nitroglycerine, RDX or nitrocellulose. The reaction is sensitive to TNB and to tetryl (2,4,6-trinitrophenylmethylnitramine) as well as to TNT. A separate calibration curve is needed for each compound.

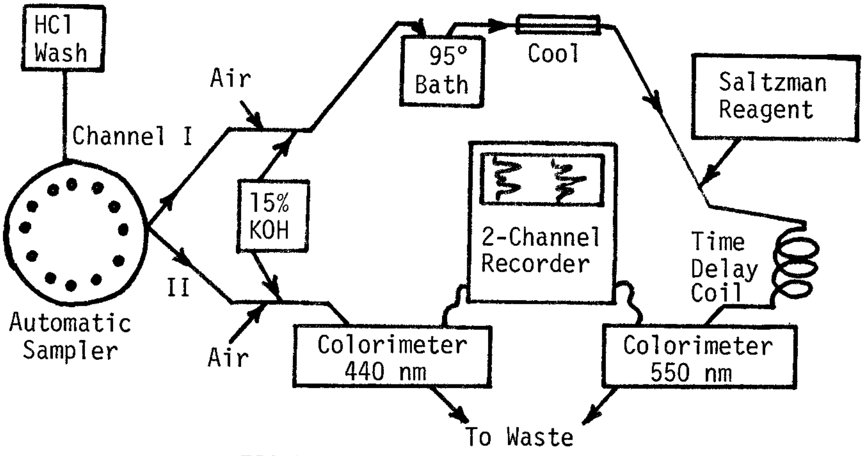

FIGURE Automated Analysis Diagram

The method is usable to 80 ppm α-TNT and the analytical working curve is linear up to 20 ppm. The reproducibility of the method is ±10% at the 1 ppm level.

In actual use for a mixed binary system containing TNT and RDX the amount of TNT determined in Channel II is used to calculate its response in Channel I. The residual intensity in Channel I is then used to estimate the amount of the second component contributing to the total absorbance of Channel I. For binary mixtures of TNT and RDX the sensitivity for RDX in Channel I was found to be 2.5 times that for TNT. The method was found to be a convenient working method for a water surveillance program for munition plants.

## References

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