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ANION EXCHANGE RESINS FOR THE DETECTION OF  
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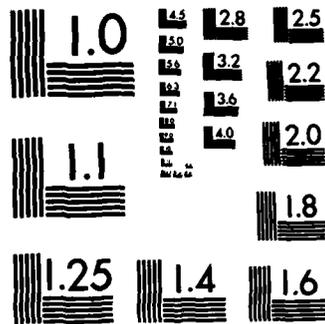
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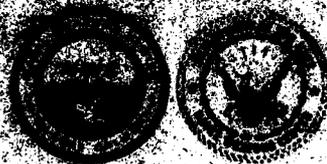
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# Anion Exchange Resins for the Detection of 2,4,6-Trinitrotoluene in Water

by  
Sterling R. Greni  
and  
Eric D. Erickson  
*Research Department*

DECEMBER 1982

NAVAL WEAPONS CENTER  
CHINA LAKE, CALIFORNIA 92085



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## FOREWORD

Most explosives and their decomposition products are toxic. Their release into the environment has to be monitored to ensure minimal harm to the environs and the population at large. In this study, a field detector has been developed to detect 2,4,6-trinitrotoluene (TNT) in effluent water. With this kit, concentrations at or below the toxic level are easily indicated.

The work described in this report took place between June 1980 and September 1981. The work was performed with Pollution Abatement Research funds, Program Element No. 62765N, NAVSEA Task Area Number SF65572391 under sponsorship of Dr. George Young and under USATHAMA Task R904.10.0263 under sponsorship of H. R. Feinberg.

This work has been reviewed for technical accuracy by C. A. Heller and E. C. Martin.

Approved by  
E. B. ROYCE, *Head*  
*Research Department*  
15 November 1982

Under authority of  
J. J. LAHR  
CAPT U.S. NAVY  
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(U) The reactions of 2,4,6-trinitrotoluene (TNT) with strongly basic anion exchange resins were examined with the ultimate goal being the development of a field detector for TNT in water. Initial work involved a study of the kinetics of the reaction of TNT with various anionic forms of anion exchange resins. The relative reaction rates observed were  $SO_4^{2-} < Cl^- < OH^- < CN^-$ . Bisectional indicator tubes were developed in which the TNT is first converted to its colored Meisenheimer anion and then trapped on an anion exchange resin. An estimate of the TNT concentration can be made by comparing stain lengths. Two indicator tubes have been developed. One for the 0.1-10.0 ppm range and another for the 30-100 ppb range. In an attempt to improve the indicator tubes, various techniques were examined for the manufacture of pellicular anion exchange resins. ←

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## INTRODUCTION

2,4,6-Trinitrotoluene (TNT) is found in the effluent water of some military ammunition plants. TNT is recognized as a blood and liver toxin which can be absorbed through the skin, lungs, or gastrointestinal tract.<sup>1</sup> Maximum discharge levels of TNT have been set by several states at 1.0 ppm. To meet these standards, ammunition plants filter their effluent water through absorption columns which consist of activated carbon or other strong absorbents.<sup>2</sup> These columns have a limited capacity for absorbing contaminants. Breakthrough (an indication that the column is saturated and should be replaced) is characterized by an increase in the outlet concentration. The outlet concentration from the columns is monitored to determine when breakthrough occurs.

Most methods available for monitoring TNT concentration in water require laboratory techniques such as reverse-phase high performance liquid chromatography, oxidation followed by colorimetric nitrate determination,<sup>3</sup> extraction into an organic phase followed by gas chromatography, polarography, or a fluorescent-dye anion exchange resin technique.<sup>4</sup> Because these techniques are time consuming, require expensive laboratory equipment, and must be performed by personnel trained in chemistry, we wanted to develop a TNT detection method which could be used in the field. This method should be rapid, require small sample volumes, be free of interferences, easy to perform, and provide no health hazard to inexperienced technicians. The TNT detection method that we have developed utilizes TNT's reaction with anion exchange resins.<sup>5</sup> This paper will detail the research and development studies on this TNT detection method. Areas of TNT chemistry studied were the kinetics of TNT's reaction with anion exchange resins, bisectonal TNT indicator tubes, and preparation of anion exchange beads without internal pores.

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<sup>1</sup> W. D. McNally. *Toxicology*. Chicago, Industrial Medicine, 1937.

<sup>2</sup> Iowa Army Ammunition Plant. *Achieving a Better Environment*. Middletown, Iowa, IAAP, 1977. (Publication UNCLASSIFIED.)

<sup>3</sup> Daniel C. Leggett. "Determination of 2,4,6-Trinitrotoluene in Water by Conversion to Nitrate," *Anal. Chem.*, Vol. 49 (1977), p. 880.

<sup>4</sup> Carl A. Heller, Robert A. McBride, and Matthew A. Ronning. "Detection of Trinitrotoluene in Water by Fluorescent Ion-Exchange Resins," *Anal. Chem.*, Vol. 49 (December 1977), p. 2251.

<sup>5</sup> C. A. Heller, S. R. Greni, and E. D. Erickson. "Field Detection of 2,4,6-Trinitrotoluene in Water by Ion-Exchange Resins," *Anal. Chem.*, Vol. 54, No. 2 (February 1982), pp. 286-289.

## EXPERIMENTAL SECTION

## KINETIC STUDY OF TNT'S REACTION WITH ANION EXCHANGE RESINS

Experimental Procedure

Three reactor types may be employed in the collection of kinetic data: a constant volume, batch-stirred reactor; a stirred-flow reactor; or a flow reactor. For this experiment, we decided to use batch and flow reactors. The batch reactor has the advantage of being easier to construct and operate than a flow reactor. The reaction rates obtained with the batch reactor are average rates over long periods of time (approximately 1.0 minute); therefore, a flow reactor was designed to measure reaction rates over a shorter period of time (1-2 seconds).

Reactor Construction. Reactor design is influenced by several conditions of the reaction (i.e., temperature and pressure), properties of the reactants, physical state of the reactants, and the amount of time and effort to be invested. The type of reaction which is discussed in this paper proved to be the overriding factor in the construction of the reactors. After taking into consideration all parameters that affect reactor design, we decided to use both a batch and a flow reactor.

*Batch Reactor Construction.* The batch reactor consisted of a fritted funnel, a side-arm flask, and a vacuum system (Figure 1). The fritted funnel allowed both mixing and separating of the TNT solution from the anion exchange resins. The side-arm flask collected the TNT solution after it had been removed from the funnel. Limitations of the batch reactor will be discussed in the experimental problems section.

*Flow Reactor Construction.* The flow reactor was used to determine reaction rates that were close to initial reaction rates. Despite the fact that the flow reactor was difficult to construct and operate, it did yield useful data. The flow reactor consisted of a 50-ml buret, an 125-ml Erlenmeyer flask, a reaction vessel, a Cole-Parmer Masterflo tubing pump, a Swage-Lok tubing coupler, and Viton tubing (Figure 2). The buret (the reservoir for the TNT solution) allowed easy calculation of the TNT solution's volumetric flow rate. Viton tubing was found to be the only type of tubing which did not absorb TNT. After pumping the TNT solution through the reaction vessel, the solution was collected in the Erlenmeyer flask.

The design of the reaction vessel had to be such that it allowed TNT solution to pass through, but still retain, the anion exchange resin. In order to accomplish this, a small, fritted funnel was converted into a reaction vessel (Figure 3). A Swage-Lok coupler was placed on one end of the reactor to facilitate loading and unloading of the resin. Problems encountered in the construction and operation of the flow reactor will be discussed in the experimental problems section.

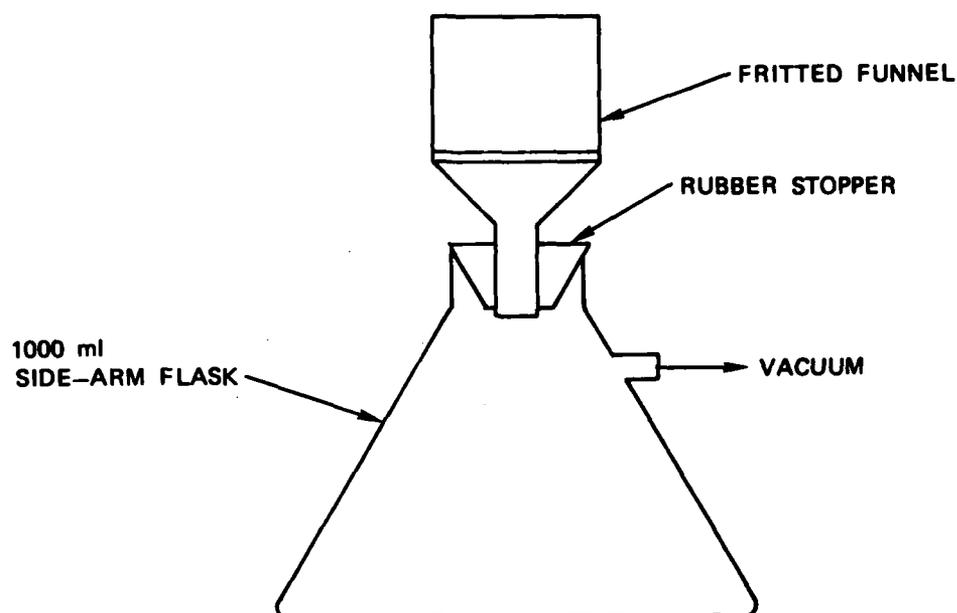


FIGURE 1. Batch Reactor.

Reactor Operation. Two sets of operating procedures had to be developed because of the use of different reactor types. The operating procedure for the batch reactor was simple and required very little time to perform. However, the kinetic data collected with the batch reactor were useful only in obtaining reaction rates that were averaged over a long period of time relative to the actual reaction rates. The flow reactor gave reaction rates that were closely related to initial rates.

*Initial Preparation.* The stock solution was prepared by dissolving 0.1 g of military-grade TNT in 1,000 ml of distilled water. From this solution, working standards were prepared with the appropriate dilutions. To prevent photodegradation of the TNT, these solutions were stored in amber bottles.

Commercially available anion exchange resins required some preparation in order to obtain the desired form for each experiment. The two resins used were Bio-Rad AG-1x10 (200-400 mesh) and Dowex 2x10 (35-65 mesh). Other resins were tested but the majority of the work was accomplished with these two resins. All of the resins used had the same basic structure (Figure 4); however, different counter-ions were prepared for our experiments (chloride, hydroxide, cyanide, fluoride, and sulfate). Since Uranine dyed resins had been used in the development of a fluorescent detector for TNT,<sup>4</sup> some of the resins were dyed with Uranine dye (a fluorescent dye) in order to see what effect, if any, the Uranine dye had on the reaction rates.

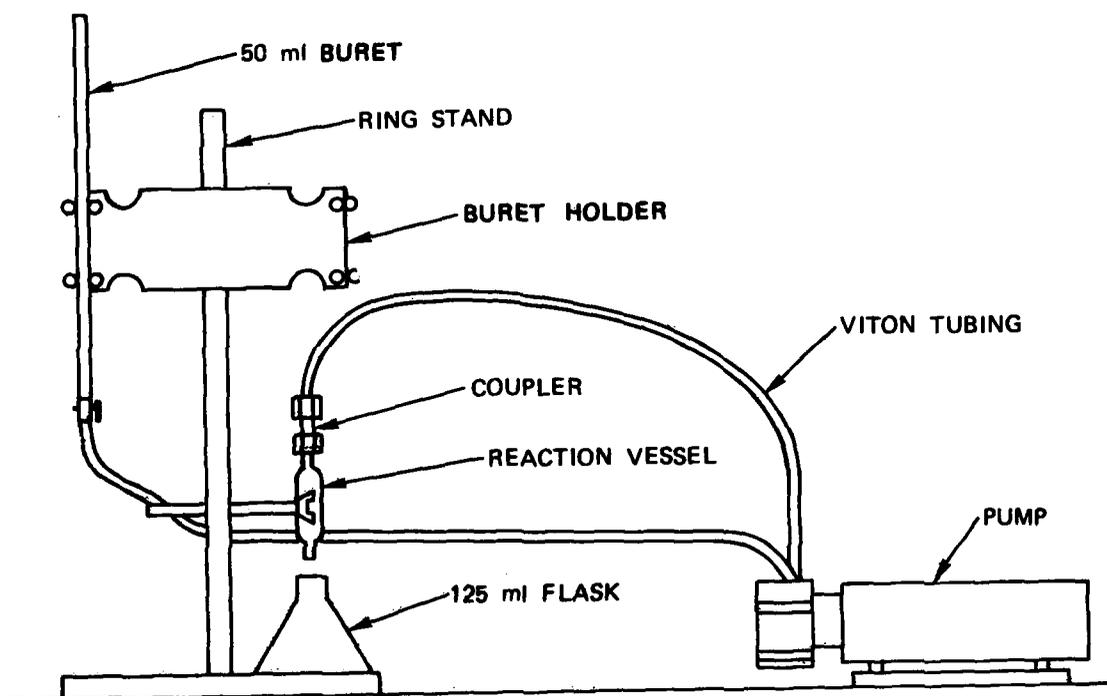


FIGURE 2. Flow Reactor.

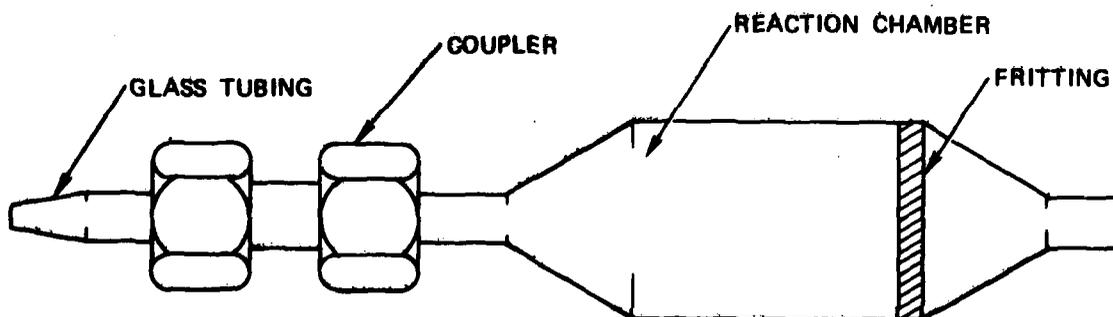


FIGURE 3. Plug-Flow Reaction Chamber.

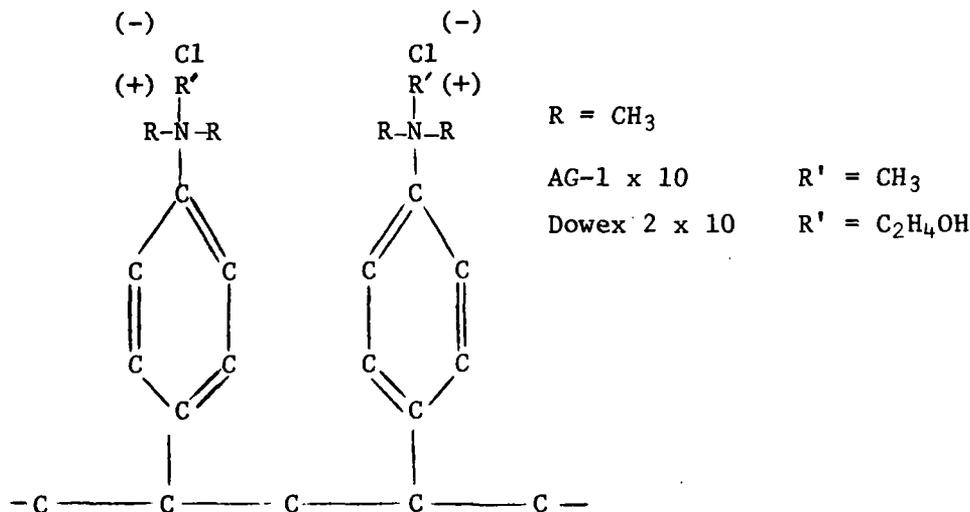


FIGURE 4. Polystyrene/Quaternary Ammonium Salt Anion Exchange Resin Structure.

Resins obtained from the manufacturer had chloride as the counter-ion. In order to test other counter-ions, the chloride ion had to be replaced by the ion of interest. This was accomplished by stirring a sample of the resin for 2-4 hours in a 1.0 M solution of the sodium salt of the specie of interest. The resin was then washed with distilled water and dried in a vacuum oven.

*Batch Reactor Operation.* The batch reactor operating procedure consists of four steps. Place 1 to 2 g of dried resin into the funnel. Add 50 ml of 5-10 ppm TNT solution to the resin. Agitate the mixture with a glass stirring rod for the duration of the reaction. Apply vacuum for 55 seconds, and remove the TNT solution from the funnel. Using a stopwatch, measure the initial and final TNT concentrations.

*Flow Reactor Operation.* Remove the reactor from the system (Figure 2) and connect a funnel to the top of the reactor with a small section of Tygon tubing. Apply vacuum to the bottom of the reactor. Dump a 1 to 2 g sample of dried resin into the funnel and wash it into the reactor with water. Use vacuum for 5-10 minutes to remove the excess water from the reactor.

After loading the reactor with the resin, connect it back into the reaction system. Next, fill the 50-ml buret with the TNT solution. Open the buret's stopcock so that the solution can flow through the system. Start the pump and let it run until 50 ml of the TNT solution is removed from the buret. At that point stop the pump and record the time the solution took to go through the system. Lastly, determine the concentration of the spent TNT solution.

Reaction Rate Calculation. In order to perform reaction rate calculations, we had to determine the concentration of initial and final TNT solutions.

*Determination of TNT Concentration.* Concentrations were determined by monitoring the absorbance of TNT solutions using a Perkin-Elmer 202, double-beam UV/Vis spectrophotometer. Quartz cells of 0.1-10 cm path length were used in the spectrophotometer. TNT exhibits a peak absorbance at 233 nm with a molar extinction coefficient of  $19,600 \text{ M}^{-1} \text{ cm}^{-1}$  at this wavelength.<sup>4</sup> TNT solutions obey Beer's Law at low concentrations. The concentrations of the TNT solutions were calculated using Beer's law and measured values of absorbance and path length.

*Calculation of Reaction Rate.* Reaction rates were calculated by dividing the difference in concentration (final concentration minus initial concentration) by the reaction time. The reaction time in the batch reactor was defined as the contact time and in the flow reactor as the mean residence time. This yielded reaction rates which were the average rate of change of TNT concentration per reaction time.

Reaction times were measured with a stopwatch. For the batch reactor, the reaction time was simply the time the TNT solution was in contact with the anion exchange resin. However, for the flow reactor the reaction time was equal to the mean residence time as calculated using equations 1 and 2:

$$V_v = (V_t - m/P)/m \quad (1)$$

$$\bar{t} = (V_v)m/\dot{V} \quad (2)$$

where

$V_v$  = void volume of the resin,  $\text{cm}^3/\text{g}$ ,

$V_t$  = total volume occupied by  $m$  grams of the resin,  $\text{cm}^3$ ,

$m$  = mass of the resin, grams,

$P$  = density of the resin,  $\text{g}/\text{cm}^3$ , and

$\dot{V}$  = flow rate of the TNT solution,  $\text{cm}^3/\text{s}$ .

The resin density was determined using a gas pycnometer. Volumetric flow rate ( $\dot{V}$ ) was determined by measuring the amount of time required for a specified volume of solution to flow from the 50-ml buret.

### Kinetic Data

Some of the parameters which affect TNT's reaction rate with anion exchange resins can be determined by examining the kinetic data. These parameters include resin mesh size, type of resin, and the resin counter-ion. As molecules of TNT contact anion exchange resins, the molecules react with the counter-ion of the resin to form colored TNT anions. These anions ionically bond to the exchange sites on the resin. Depending on the counter-ion used, different colors and reaction rates were observed. Other parameters such as resin type, mesh size, and amount of resin affect reaction rate.

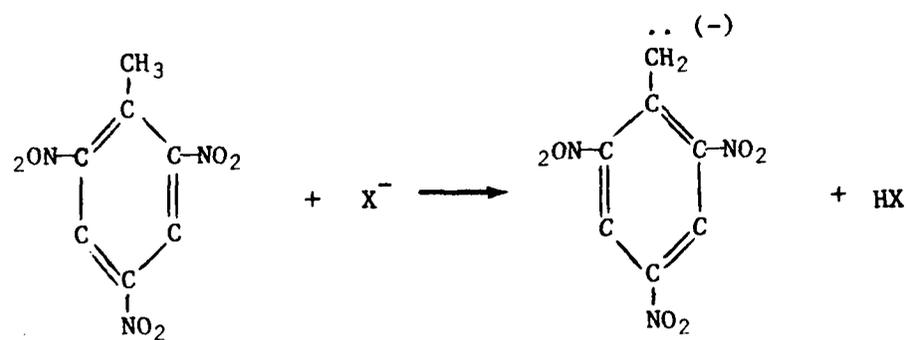
TNT Reactions. Counter-ions from the resin react with TNT molecules to form colored TNT anions. In order for a TNT molecule to form the colored anion, the molecule must drift close enough to the reaction site on the resin to react with the counter-ion. The TNT anion ionically bonds to the reaction site of the resin. Counter-ions can react with a TNT molecule, either as a nucleophilic addition or a proton abstraction.<sup>6</sup> Different colors are observed with the use of different counter-ions (Figure 5) (i.e., hydroxide counter-ion produces a purple color, while cyanide and chloride counter-ions produce a purplish-pink color). In order to determine which anion structure was produced by which counter-ion, spectra were obtained using the techniques of solid-state electronic spectra and Fourier Transform Infrared spectrophotometry (FTIR). Neither technique provided any conclusive evidence as to which anionic structure was produced by which counter-ion.

Batch Reactor Data. Batch reactor experiments were performed using Bio-Rad AG-1x10 (200-400 mesh) anion exchange resin with chloride or hydroxide as the counter-ions. Reaction time and initial TNT concentration were both constant while varying the amount of resin. The results of these experiments are tabulated in Table 1 and plotted in Figure 6.

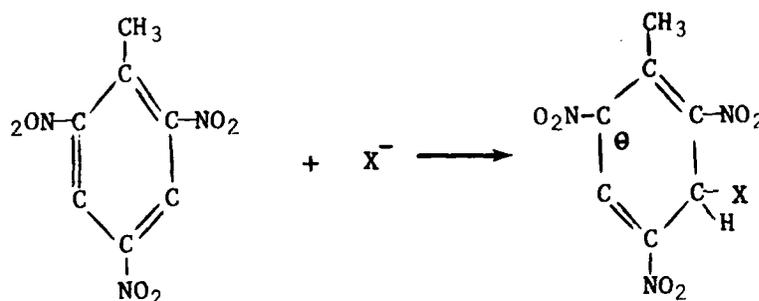
As can be observed from Figure 6, the reaction rate increases by increasing the amount of resin present. However, the rate per gram of resin decreases over the same interval. This suggests that as the amount of resin is increased, the reaction rate will approach a specific value asymptotically. The rate of reaction is faster for hydroxide than for chloride counter-ions. Reaction rates obtained with the batch reactor were average rates.

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<sup>6</sup> C. A. Fyfe and others. "Flow Nuclear Magnetic Resonance Investigation of the Transient and Stable Species Formed by the Attack of Alkoxide Ions on 2,4,6-Trinitrotoluene," *J. Amer. Chem. Soc.*, Vol. 98 (1976), p. 6983.



Proton Abstraction



Nucleophilic Addition

FIGURE 5. Colored TNT Anion Structures.

TABLE 1. Reaction Rate vs. Bead Concentration.

Type of counter-ion	Bead concentration (g/50 ml)	Reaction rate ( $\mu\text{M/s}$ )	Reaction rate/g ( $\mu\text{M/g}\cdot\text{s}$ )
Chloride	0.50	102	204
Chloride	1.00	148	148
Chloride	2.00	204	102
Chloride	3.00	242	80.7
Chloride	5.00	278	55.6
Hydroxide	0.50	144	288
Hydroxide	1.00	296	296

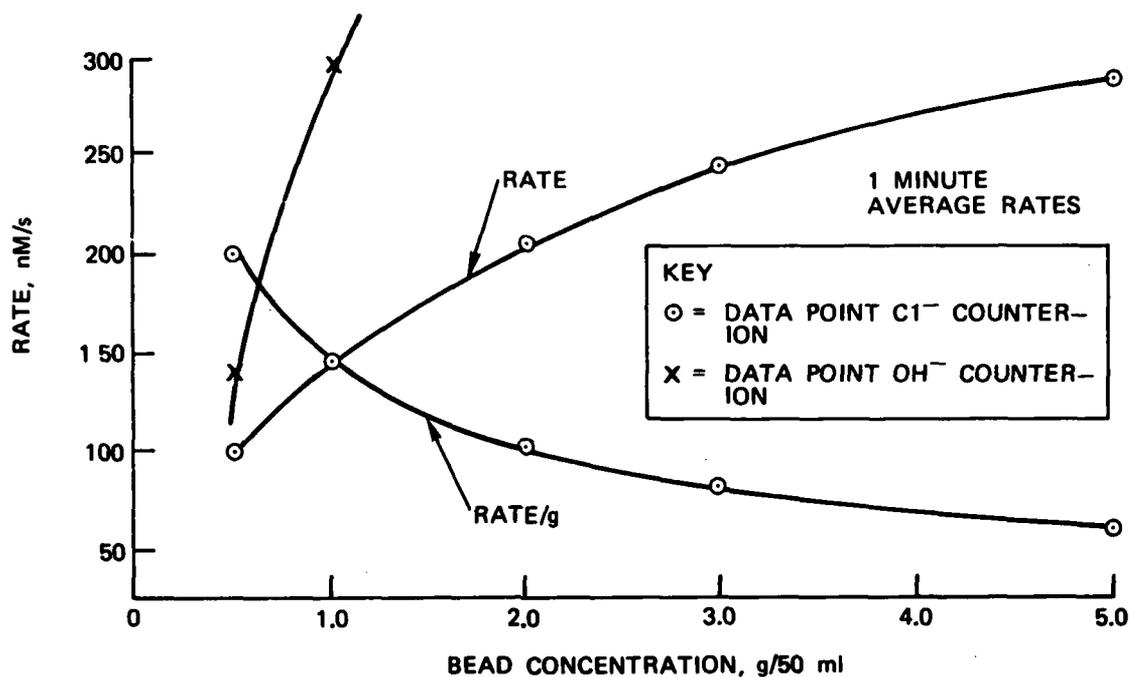


FIGURE 6. Reaction Rate vs. Bead Concentration.

Flow Reactor Data. The flow reactor system was built in order to reduce the reaction time between TNT and the resin. The reaction time was reduced to measure reaction rates which were close to initial rates. Two experiments were carried out with the flow reactor. First, an experiment was designed to test the effect of residence time on reaction rate. This was accomplished by holding all parameters constant except residence time which was varied from 0.5-1.5 seconds. Bio-Rad AG-1x10 (200-400 mesh) resin with hydroxide as the counter-ion was used in this experiment. The results of this experiment are tabulated in Table 2 and plotted in Figure 7.

TABLE 2. Reaction Rate vs. Residence Time.

All anion-exchange resin samples were 1.0 g with an hydroxide counter-ion.

Residence time (seconds)	Reaction rate ( $\mu\text{M/g}\cdot\text{s}$ )
0.369	18.07
0.891	16.60
1.11	14.63
1.23	13.37
1.49	14.29
1.53	13.92

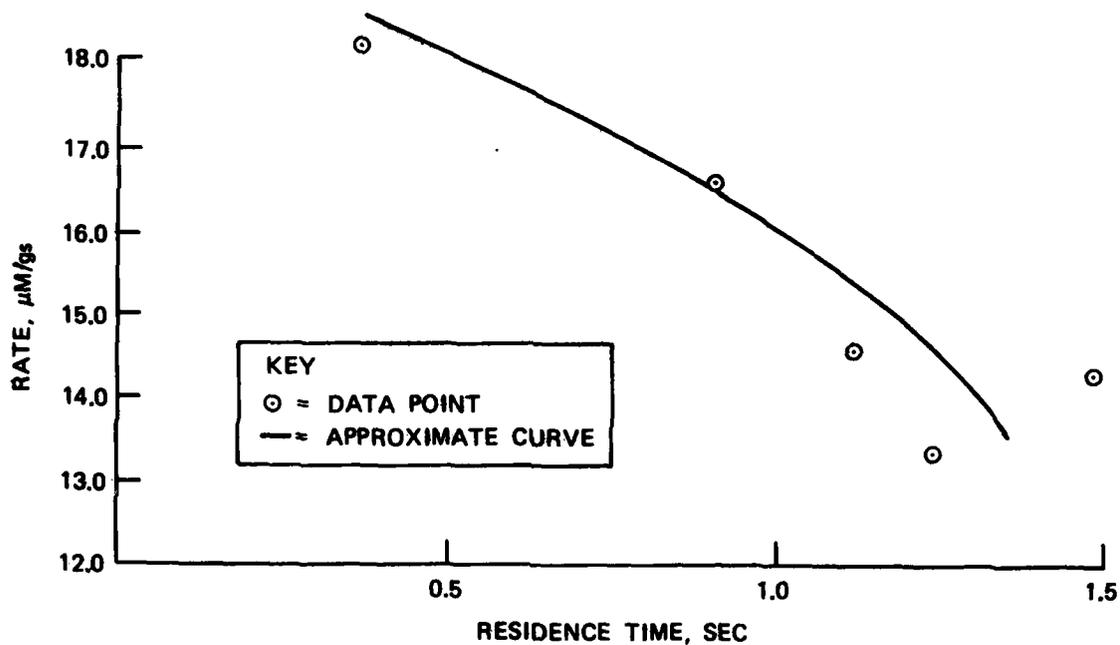


FIGURE 7. Reaction Rate vs. Residence Time.

By examining Figure 7 one can see that as the residence time increases, the reaction rate decreases. As time increases, the amount of available anion exchange reaction sites decrease, thus decreasing the reaction rate.

A second experiment was designed to determine the effect of various resin types on the rate of reaction. This experiment was performed by holding the residence time and the amount of resin constant while using different resin counter-ions. The objective was to determine which counter-ion produced the quickest rate of reaction with the TNT solution. The results of this experiment are listed in Table 3. We concluded that of those counter-ions tested the cyanide counter-ion has the highest rate of reaction and that Uranine dye had no effect on the reaction rate.

TABLE 3. Reaction Rate vs. Type of Anion Exchange Resin.

The anion exchange resin used was Bio-Rad Ag-1x10 (200-400 mesh). All samples were 1.0 g with the same residence time.

Ion exchange resin type	Reaction rate ( $\mu\text{M/g}\cdot\text{s}$ )
$\text{Cl}^-$ counter-ion	14.72
$\text{Cl}^-$ counter-ion dyed $10^{-3}$ M Uranine	15.26
$\text{OH}^-$ counter-ion	16.86
$\text{OH}^-$ counter-ion dyed $10^{-3}$ M Uranine	16.10
$\text{CN}^-$ counter-ion	40.81
$\text{CN}^-$ counter-ion dyed $10^{-3}$ M Uranine	40.08
$\text{SO}_4^{-2}$ counter-ion	7.51

#### Experimental Problems

In the course of this work many problems were encountered. Some of the problems were solved while others remain unanswered.

Batch Reactor Problems. Problems encountered in the operation of the batch reactor include:

1. Evaporation of water from the TNT solutions occurred when a vacuum was applied in order to pull the solution past the resin. This caused the final TNT solution to be concentrated. As a result, the measured reaction rates are lower than the actual rates.

2. The technique used to detect TNT concentration was sensitive to impurities. Approximately every third run was destroyed by an unknown impurity.

3. The fritted funnel clogged after repeated runs, altering the flow rate and path of the TNT solution. Unclogging the funnel required that the funnel be baked overnight in an annealing oven. It was necessary to repeat this heat treatment once a week.

4. The batch reactor could only be used to measure average reaction rates over relatively long time intervals. The flow reactor was designed to measure reaction rates over shorter time intervals.

Flow Reactor Problems. Problems encountered in the operation of the flow reactor include:

1. It was difficult and time consuming to load the resin into the reaction vessel.

2. The reaction vessel was susceptible to clogging and required heat-treating every third day.

3. Most couplings tested absorbed TNT. It was necessary to use a stainless steel Swage-Lok coupling to avoid this problem.

4. An unknown impurity interfered with the analysis of TNT concentration in about every third run. We were unable to determine the origin or identity of the unknown impurity.

5. It was time consuming to operate the flow reactor system compared to the batch reactor system.

#### BISECTIONAL TNT INDICATOR TUBES

The ultimate goal of this project is the development of a simple instrument capable of detecting low-level TNT concentrations in the aqueous effluent from ammunition plants. After consideration of both the technical background of the ultimate users of the instrument and the wide variety of locations where the effluent would be sampled and analyzed, the following criteria have been selected for this detector.

1. The instrument must detect aqueous concentrations of TNT below the regulatory limit, which is currently set at 1.0 ppm.

2. Chemical species normally present in the effluent water must not interfere with the detection of TNT.

3. In order to perform on-site analyses, the instrument must be portable.

4. The time required to perform an analysis needs to be short. Ideally, only a small sample volume should be used.

5. The operator should need very little technical training in order to operate the instrument and to obtain meaningful and reproducible results from it.

6. Finally, the instrument should not provide a health hazard to inexperienced technicians.

Development of a TNT field detection kit which meets these criteria is being carried out at the Naval Weapons Center.<sup>5</sup> As shown in Figure 8, this kit consists of a syringe, a syringe pump, a combination Swage-Lok and Luer-Lok coupler, indicator tubes, and a set of standard TNT solutions. TNT concentrations are determined by measuring the length of colored stain produced by a known volume of the unknown solution and comparing it to the length produced by a standard TNT solution obtained under the same conditions. This technique is capable of reproducibly detecting TNT concentrations as low as 0.1 ppm.

The heart of this detection device is the indicator tube. It consists of a basic oxide pretreatment section and an anion exchange resin indicator section which are separated and held in place by glass wool plugs (Figure 9). The TNT is converted to its colored Meisenheimer anion by the action of hydroxide in the pretreatment section. This anion is then absorbed onto the anion exchange resin in the indicator section to form a reddish stain whose length is proportional to the TNT concentration, the flow rate, and the sample volume.

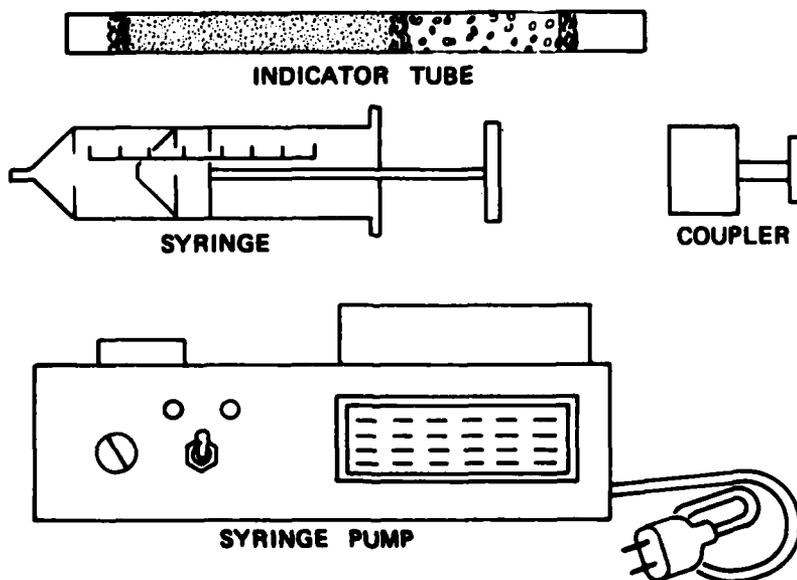


FIGURE 8. TNT Field Detector Kit.

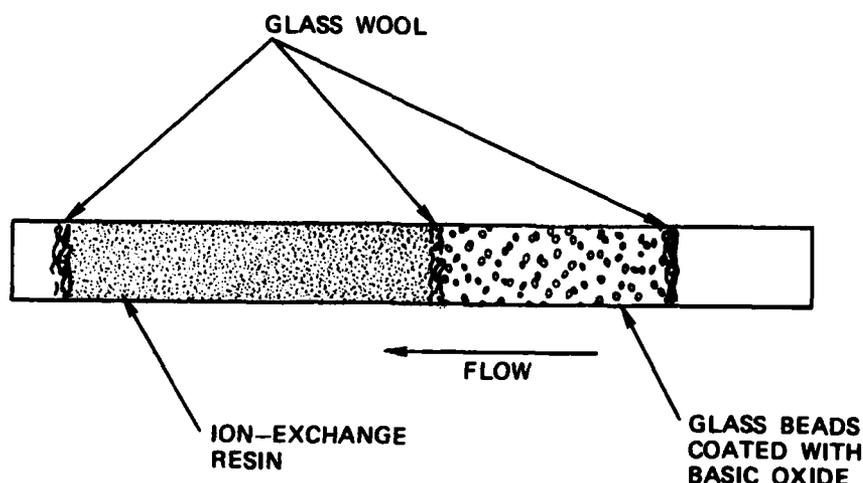


FIGURE 9. Indicator Tube.

#### Basic Oxide Presection

Any base which is strong enough to react with TNT to form the colored Meisenheimer anion could be used to pretreat the sample. In order to reduce the risks from exposing untrained technicians to a strong base and to improve the simplicity of the method, we decided that the base should be incorporated into the indicator tube. To prevent the base from being carried downstream with the first surge of water, the base chosen must have a low solubility in water. Good results have been obtained using calcium oxide (CaO) as the base.

Indicator tubes which have CaO mixed with the anion exchange resin tend to yield long, diffuse stains. It is believed that this effect is caused by the formation of the Meisenheimer anion as the TNT progresses through the tube. This effect is alleviated by placing a basic presection in front of the indicator section in order to convert the TNT to its Meisenheimer anion before contacting the anion exchange resin. This produces a stain in the indicator section whose length is shorter but much more readily discernable.

Calcium oxide is a very fine powder. When used as the presection in the indicator tubes, CaO causes large back pressures to occur in the system. This causes leaks in the system which reduces knowledge of both sample volume and flow rate. Since the stain length is dependent on both these factors, it was necessary to reduce the back pressure. This was done by coating inert glass beads with CaO. The following method is used to obtain a uniform coating of CaO on glass beads.

1. Prepare a mixture which is 0.6% CaO and 94% glass beads (0.2-1.0 mm).

2. Add water to make a paste of the mixture.
3. Dry the mixture in a vacuum oven.

### Indicator Section

Any strongly basic anion exchange resin which is light in color could serve as the indicator section in the tube.

Dowex 1x10 is the anion exchange resin which is presently being used in the TNT indicator tubes. However, manufacture of Dowex 1x10 has been discontinued. Numerous resins were tested as a possible replacement for Dowex 1x10. Those resins tested include Bio-Rad AG-3, Cellex-T, Cellex-QAE, Amberlyst A-26, Amberlite IRA 400, Amberlite IRA 401, Dowex 2x4, and Dowex 1x8. None of these resins proved to be suitable for use in the TNT detector. Some of the resins, such as Dowex 1x8, turn a reddish color when they come in contact with hydroxide ions. Excess hydroxide, produced by the basic oxide section, masked the color change produced by the TNT.

Personnel at Bio-Rad Laboratories\* thought that the hydroxide discoloration of the anion exchange resins was a quality control problem and was limited to certain batches of resin. The reason the resins change color is not understood but the problem is being studied by Bio-Rad. The laboratory recommended using Bio-Rad AG MP-1, a macroporous resin, as a replacement for Dowex 1x10. Hydroxide does not discolor AG MP-1 and its white color facilitates detection of the TNT stain. Therefore, AG MP-1 was chosen as a replacement for Dowex 1x10.

### Chemical Interferences

Various compounds were tested to determine which would interfere with the TNT analysis. Among the species which did not interfere are "pink" water, tap water, cyclotrimethylenetrinitroamine (Royal Development Explosive (RDX)), acetone, ethanol, and toluene.<sup>6</sup> The compounds which interfere are sodium chloride, potassium chloride, sodium nitrate, ammonium chloride, ammonium nitrate, and various acids. Acids interfere with the TNT determination by neutralizing the base in the basic oxide section.

Salt water prevents TNT detection by interfering with the action of the base in the basic oxide section. It is believed that the increase in ionic strength causes an increase in the solubility of the basic oxide. Thus, all the basic oxide is washed off the glass beads before it can react with the majority of the TNT. Salt water interference is

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\* Telephone conversation with Roy Wood of Bio-Rad Laboratories on 7 July 1981.

overcome by utilizing a mixture of bases with varying solubilities. The mixture which we have chosen to eliminate salt water interference is composed of 1.0% CaO, 1.0% BaO, and 2.0% Mg(OH)<sub>2</sub> mixed with 96% glass beads. A normal stain is produced by 1.0 ppm TNT in 1.0 M NaCl when using this mixture of bases. By mixing the bases together, one produces a base which can maintain a somewhat constant solubility over a wide range of ionic strengths.

#### Low Concentration Indicator Tubes

A TNT indicator tube has been constructed which is capable of detecting TNT concentrations as low as 0.02 ppm with a 10 cc sample volume. This represents an order of magnitude increase in sensitivity over the old indicator tubes. The new indicator tube consists of 0.4 g basic oxide coated glass beads (mixed base), 0.15 g Bio-Rad AG-1x10 (200-400 mesh) anion exchange resin, and a 10-cm-long piece of capillary tubing (0.146 cm inner diameter, 0.735 cm outer diameter).

Various tests were conducted on the new indicator tubes including flow rate and detection limit tests. Flow rates from 1.0 to 2.7 ml/min were tested. At flow rates greater than 1.5 ml/min the TNT stain became noticeably less distinct. Thus, any flow rate greater than 1.5 ml/min will reduce the detection limit of the indicator tubes. In order to determine the detection limit, 10-ml TNT samples of concentrations 0.1-0.01 ppm were run through the indicator tubes. The results of these tests are in Table 4. Concentrations as low as 0.02 ppm can be detected by inexperienced personnel using this tube.

Two major limitations exist with this new indicator tube. First, the indicator tube is only good for low concentrations (0.1 ppm and less); at higher concentrations the stain grows darker rather than longer. Second, because of the small resin size and small tube diameter, the back pressure produced by this tube is much greater than the previously described indicator tube. Therefore, the back pressure limits the size of sample volume which can be used and the flow rate at which the sample can be run.

TABLE 4. Stain Length vs. Concentration  
for Low Level Indicator Tubes.

Concentration (ppm)	Stain length (mm)	Observations
0.1	5.0	Light reddish color
0.03	3.0	Faint, but easily detectable
0.02	2.0	Very faint, careful observation required
0.01	---	Almost undetectable, very careful observation required

#### PREPARATION OF PELLICULAR ANION EXCHANGE BEADS

Using conventional anion exchange resins, stain length does not vary linearly with TNT concentration. This nonlinearity is due to diffusion of the TNT anion into the pores of the resin. The greater the TNT concentration, the faster the anion is able to diffuse into the resin causing the stain to grow darker instead of longer. This problem can be eliminated with the use of resins with surface exchange sites on an impermeable core (pellicular resin). The advantages of surface active resins are longer stain length, more linear response, and possibly greater sensitivity.

#### Procedures of Manufacture

Several methods were tested to produce surface active resins. The goal was to coat finely ground resins on an inert solid core. First, the resin was ground with dry ice using a Grindex steel ball MBR pulverizer. Next, the ground resin was sieved to the desired size range.

Anion Exchange Resin Coated on Glass Beads Using Polyvinyl Acetate as the Binder. The first coating method entailed coating glass beads with polyvinyl acetate (PVA) and then coating the glass beads with powdered resin. This method was accomplished using the following procedure:

1. Dissolve PVA in methanol (5% solution).
2. Add a measured quantity of glass beads to the PVA solution.

3. Precipitate the PVA onto the glass beads, by the addition of water.
4. Separate the glass beads with the use of a 30-mesh screen.
5. Place PVA-coated glass beads in a vial with a large excess of ground anion exchange resin.
6. Heat the vial for 1-5 minutes while it is being shaken. Care must be taken not to overheat the vial and scorch the resin.
7. Remove the excess resin by sieving the mixture with a 60-mesh screen.

Experiments were conducted using PVA solutions ranging in concentration from 1-5%. Best results were obtained with a 2.0% solution of PVA, yielding a glass bead surface coating of approximately 20%. However, this method was unsatisfactory because the coating was neither uniform nor reproducible.

Anion Exchange Resin Coated on Polyvinyl Acetate Spheres. The second method consisted of applying a resin coating directly to PVA spheres. The procedure used was:

1. Obtain the desired PVA sphere size range through sieving.
2. Place the PVA and the powdered resin in a vial (using a large excess of resin to prevent agglomeration of the PVA).
3. Heat the mixture while shaking. The heat was applied with a heat gun and the mixture was agitated with a wrist action shaker.
4. Allow the mixture to cool and remove the excess resin with 60-mesh screen.

The thickness of the resin coat can be controlled by the amount of heat applied. A thicker coat was obtained by applying more heat. Again, care must be taken not to scorch the resin or melt the PVA. Various size ranges of PVA were tried. The best results were obtained with 30-60 mesh PVA spheres.

Anion Exchange Resin Coated on Glass Beads Using Clear Spray Lacquer as the Binder. The third coating method consisted of coating glass beads with crushed resin using a clear spray lacquer as the binder. The procedure was:

1. Place a quantity of glass beads in a round-bottom flask.
2. Spray the beads with lacquer.

3. Dilute the mixture with toluene.
4. Evaporate to dryness using a rotary evaporator.
5. Sieve the glass beads through a 30-mesh screen.
6. Mix coated glass beads with excess resin in a vial.
7. Heat and shake the vial.

The best coating was obtained with 8.0 g of glass beads and 3.0 sec of lacquer spray in a 40 ml solution.

#### Method Chosen

Numerous parameters affect the performance of these surface-activated anion exchange resins. The size range of the ground resin has an effect on the stain length and linearity of the response. The best results were obtained with resin ground to less than 400 mesh. The main advantages of resin coatings are longer stain lengths (i.e., 1.0 ppm TNT sample; coated resin indicator gave a stain length of 90 mm while a conventional resin indicator gave a stain length of 8.0 mm) and greater porosity which decreases back pressure. The disadvantages of resin coatings are that it is difficult to obtain a uniform, reproducible coating, the end-point of the stain is not definite, reduced sensitivity (concentrations of 0.1 ppm TNT cannot be detected), and the anion exchange resin is difficult to grind. Of the three coating methods investigated, anion exchange resin coated directly on PVA proved to be the best. This method is quick and easy to perform and its response to TNT concentration is most nearly linear (Figure 10).

#### CONCLUSIONS

Two different reactor types were designed to study the kinetics of the reaction of TNT and a quaternary amine anion exchange resin. The batch reactor works best for determining rates which require large contact time. The flow reactor is used for samples requiring small contact time and worked best for this study.

The rate of reaction between TNT and an anion exchange resin is dependent on the counter ion in the resin. Rates observed varied from a low of 7.51  $\mu\text{M/g}\cdot\text{s}$  for  $\text{SO}_4^{2-}$  to 40.8  $\mu\text{M/g}\cdot\text{s}$  for  $\text{CN}^-$ . Relative reaction rates observed were  $\text{SO}_4^{2-} < \text{Cl}^- < \text{OH}^- < \text{CN}^-$ .

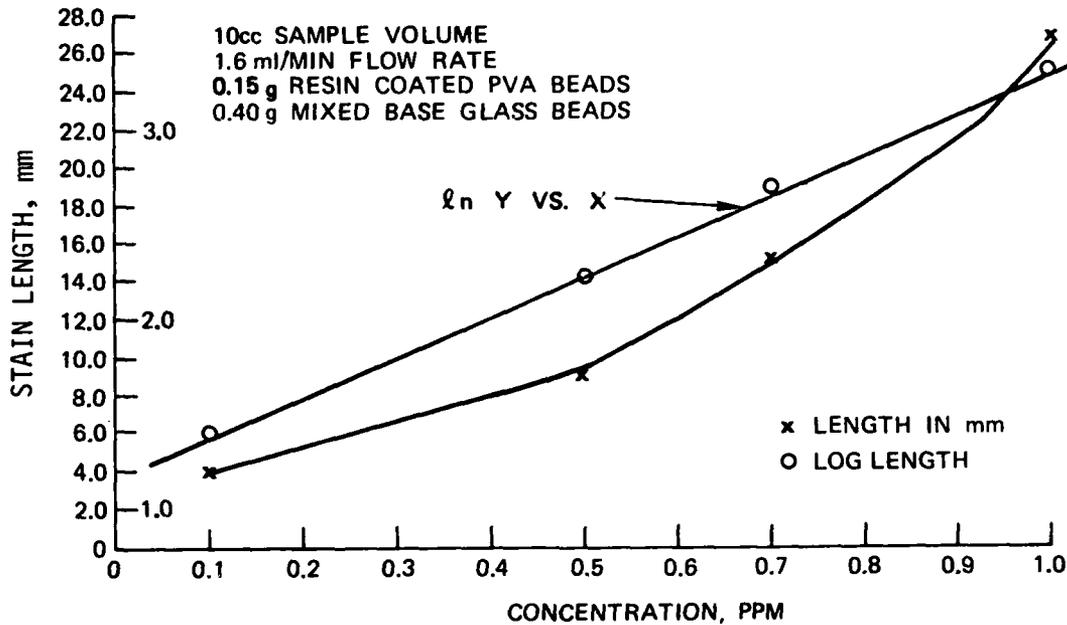


FIGURE 10. Stain Length vs. Concentration.

The kinetics data were obtained using resins which are no longer manufactured. These data were also obtained for TNT rather than the TNT Meisenheimer anion which is used in the indicator tubes. In order to better understand the reactions occurring in the indicator tubes and possibly improve these tubes, it may be necessary to repeat the kinetic study using AG MP-1 resin and the TNT Meisenheimer anion.

The TNT field detection kit which has been developed is workable at the present time; however, further refinement is necessary before the kit will be ready for military use. An understanding of the chemistry involved in the reaction of anion exchange resins with TNT could facilitate the refinement of the detector kit. Among the possible approaches to this investigation are solid state NMR, solution NMR (using compounds such as benzyltrimethylammonium chloride or triton B to simulate the reaction sites of the ion exchange resins), photoacoustical ultraviolet-visible spectrophotometry, and Fourier Transform Infrared spectroscopy using photoacoustics or diffuse reflectance. Another possible way to improve the indicator tubes is with the use of low-capacity anion exchange resins. Finally, further research to improve the linearity of the response needs to be conducted in the area of surface active resins and their production.

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