

THE USE OF POLYANION-STABILIZED DIAZONIUM  
CATIONS AS ANALYTICAL REAGENTS

by

VERNON EUGENE CATES

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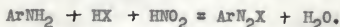
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## INTRODUCTION

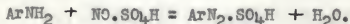
When a cold solution of a primary aromatic amine is treated with nitrous acid a diazo-compound is formed. Peter Griess, at Marburg, Germany, in the year 1858, was the first to prepare and recognize this group of compounds. He named his new compound "diazo" because he believed two nitrogen atoms had replaced two atoms of hydrogen.

The most used reaction for synthesis of diazo-compounds is generally expressed as follows:



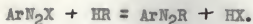
The Ar is an aromatic radical, HX is a strong acid, and  $\text{ArN}_2\text{X}$  is the diazo-compound or diazonium salt. When the aromatic nucleus has an electron attracting group substituted on the same ring with the diazo-group the compound ionizes to a considerable extent in water to form  $\text{ArN}_2^+$ , diazonium, and  $\text{X}^-$  ions.

The basis of one of the other main methods for synthesis of diazonium compounds is the reaction of nitrosylsulfuric acid upon the aryl amine, thus:



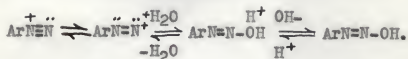
Other methods are known for the preparation of diazonium salts, but these are the most used reactions. Details and descriptions of other reactions may be found in Saunders (3).

The usual coupling reaction of diazonium salts with amines and phenols can be shown by the general equation from Saunders (3), p. 194, as:

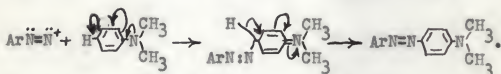


The R is any aromatic phenol, or amine.

Saunders (3), p. 231, reviewed the work of Hauser and Breslow who propose the following equilibrium series in terms of the resonance theory (dots represent electrons):



From this series was selected  $\text{ArN}=\ddot{\text{N}}^+$  as the active form for the diazonium salts. They then denote the mechanism of coupling of the diazonium ion with dimethylaniline as occurring thus:



The diazonium compounds find extensive use in the manufacture of dyes due to their ability to couple with aromatic amines and aromatic hydroxy compounds to form colored derivatives. They are used in synthesis by eliminating the diazo-group or by replacing it with another group or radical. Also, the aryl nucleus to which the diazo-group is attached may be substituted without affecting the diazo-group, thereby finding use in the synthesis of aryl compounds with specially oriented groups. In this paper attention was focused upon the first use and the application of dye formation for analytical purposes.

Numerous methods of colorimetric analysis have been developed using the diazonium salts in reactions with amines and phenols to produce colored dyes. The American Public Health Association

(5) had a tentative method based on the diazonium salt-phenol reaction for analysis of phenols in water. Snell and Snell (4) listed a number of determinations with diazo-salts. The usefulness in chemical analysis of the diazonium salts is suggested by these analytical schemes and the possibilities of further developments.

One of the deterrents of using diazonium salts as an analytical reagent is their lack of stability. Extreme care is necessary for the safe handling of dry diazonium salts due to their tendency to explode when heated or jarred. From the first work by Griess many instances of damage caused by explosions of diazonium salts have been reported. In solution or when wet, and when exposed to light the salts decompose with elimination of nitrogen. Saunders (3), p. 61, reviewed work on the rate and mechanisms of decomposition in aqueous solution. Redd (2), Vol. III A, p. 265, reported that the order of explosibility of the diazonium salts to be; sulfate is less than chloride is less than nitrate is less explosive than perchlorate.

Listed by Venkataraman (6), p. 217, in order of decreasing stability of their chlorides are such diazonium ions as p-chlorobenzenediazonium chloride, m, o, and p-nitrobenzenediazonium chloride, p-sulfonic acid benzene diazonium chloride, alpha and beta-naphthyldiazonium chloride, and benzene diazonium chloride. He states that the stability of the diazonium salt is increased by the substitution of electronegative groups on the

nucleus. Also, the stability of benzenediazonium chloride is decreased by m-hydroxy, o-methyl, m-methyl, m-methoxy, o-phenyl, and m-phenyl substitution. Substitution by chlorine, carboxyl, sulfonic or nitro groups increases the stability, as well as substitution by methoxy, hydroxyl, phenyl or methoxyl in positions other than those just mentioned.

Methods have been sought which will stabilize the diazo-compounds so they can be transported and stored in a dry, ready-to-use state with reasonable safety. According to Saunders (3), p. 72, the first method developed used evaporation of an acid solution of diazo-compound under vacuum at a temperature not over  $45^{\circ}\text{C}$ , and then binding the remaining water as water of crystallization by adding anhydrous salts, such as sodium sulfate or aluminum sulfate. The solid mass could then be ground, standardized, and passed into commerce. Other stabilized diazo-compounds are made by diluting the solid compound with some inert, solid salt that binds any water remaining with the diazonium salt.

Another method of stabilization utilizes the ability of diazonium salts to form double salts with a number of metallic salts. Examples of such double salts found in Rodd (2), Vol. III A, p. 265, and Saunders (3), pp. 72 and 76, are  $\text{ArN}_2\cdot\text{F}\cdot\text{BF}_3$  for complex anions, and  $\text{ArN}_2\text{Cl}\cdot\text{ZnCl}_2$  or  $\text{ArN}_2\text{Cl}\cdot\text{PtCl}_2$  for simple anions.

The purpose of the investigation here undertaken has been to develop further methods of stabilization that will make the



diazonium compounds more convenient analytical tools. Two methods of stabilization were studied. The first involved dispersion of the diazonium ion upon cation exchange resin from which the diazonium ion could be readily released into solution by ion exchange for reaction with a solution of an aromatic amine or hydroxy compound. The second method involved diazonium ions chemically anchored to filter paper to form spot-test papers which could be used for qualitative analysis by applying a drop of a solution containing an aromatic amine or hydroxy compound. Most of the work involved qualitative tests, but some of the quantitative aspects were also studied. Included in this work were 33 diazonium salts which were used to treat IR-120(H) ion exchange resin, and also eight variations of spot-test paper.

## EXPERIMENTAL

### Apparatus and Chemicals

Beckman Model DU Quartz Prism Spectrophotometer.

Amberlite IR-120(H) synthetic cation exchange resin, analytical grade, Rohm and Hass Co.

Filter paper, Whatman No. 42, ash free, 7 cm, circles.

Aluminum or stainless steel standard measuring spoons.

Aromatic hydroxy and amine compounds, purest available grades, or those prepared in the laboratory.

Acetic anhydride, reagent grade.

Anthranilic acid, Eastman, recrystallized.

p-Arsanilic acid, Eastman.

Acetic acid, glacial, reagent grade.

Hydrochloric acid, concentrated, reagent grade.

Nitric acid, concentrated, reagent grade.

Sulfuric acid, concentrated, reagent grade.

Dipotassium hydrogen phosphate, trihydrate, reagent grade.

Potassium hydroxide, pellets, reagent grade.

Potassium chloride, reagent grade.

Sodium hydroxide, pellets, reagent grade.

Sodium acetate, trihydrate, reagent grade.

Sodium carbonate, anhydrous, reagent grade.

Sodium nitrite, reagent grade, minimum assay 97%.

Aluminum nitrate, reagent grade.

Bismuth nitrate, reagent grade.

Cerium nitrate, reagent grade.

Lanthanum nitrate, reagent grade.

Stannic nitrate, reagent grade.

Thorium nitrate, reagent grade.

Yttrium nitrate, reagent grade.

Zirconyl chloride, octahydrate, Fisher, purified grade.

#### Buffer Solutions

pH 5, 1 M sodium acetate and 1 M acetic acid. Use 68.0 grams of sodium acetate trihydrate and 28.8 ml. of glacial acetic acid per 500 ml. of solution. The measured pH with diazonium ion solution added was 4.8.



pH 7, 2 M ammonium acetate. Use 77.1 grams per 500 ml. of solution. The measured pH with diazonium ion solution added was 6.8.

pH 9, 2 M-dipotassium hydrogen phosphate. Use 228 grams of dipotassium hydrogen phosphate trihydrate per 500 ml. of solution. The measured pH with diazonium ion solution added was 8.8.

pH 12, 1 M sodium carbonate. Use 106 grams of sodium carbonate, anhydrous, per 500 ml. of solution. The measured pH with diazonium ion solution added was 12.5.

Distilled water was given a pH of 1.8 by the solution of diazonium ion released from the sulfonic acid cation resin.

#### Preparation of Diazonium Ion Resins

For the general preparation of the diazonium salt solutions the procedures of Fierz-David and Elangey (1), modified as necessary, for the various classes of amines, were used.

The amine salt was dissolved in mineral acid such as HCl, with heating if necessary. Ice was added and a solution of sodium nitrite which had been previously cooled below 10° C, was added with vigorous stirring for diazotization. The mixture was allowed to stand in an ice bath for 10 to 15 minutes, at which time it was filtered and added to the acid form ion exchange resin fresh from the manufacturers bottle which had been washed by decantion 4 or 5 times. The mixture was stirred for about five minutes and then washed six or seven times by

decantion. The resin was partially dried on a Buchner funnel with suction for an hour, spread out in a large crystallizing dish and allowed to air dry thoroughly in the dark, preferably overnight, until the particles no longer stick together. The dry resin was then put in a well stoppered bottle and stored in the dark.

When analytical use was to be made of the diazonium ion,  $\frac{1}{2}$  level teaspoon of potassium chloride and 50 ml. of distilled water was added to 1 level teaspoon of the resin, thus freeing the ion into solution. All the diazonium ions prepared were colorless, but those having nitro groups in the ortho position underwent hydrolysis rapidly to form a yellow solution.

Of the 33 diazonium ions prepared, 3 were chosen as being the most satisfactory. The preparation of these are given here.

Preparation of 2,5-Dichlorobenzenediazonium Ion Resin. In a solution of 20 ml. of concentrated hydrochloric acid and 80 ml. of water, 6.48 grams (0.04 mole) of 2,5-dichloroaniline was heated until it dissolved. The solution was cooled to room temperature under a running water tap with constant shaking and 40 grams of ice was added. To this 2.84 grams (0.04 mole) of 97 per cent assay sodium nitrite dissolved in 40 ml. of distilled water were added slowly with constant stirring until all of the precipitated salt had gone into solution. After standing in an ice bath for 10 to 15 minutes, the solution was filtered and added to 100 ml. (dry measure) of Amberlite IR-120(II) resin that had been well washed by decation as previously described.

After five minutes contact time with stirring, the resin was washed seven times by decantation with distilled water, filtered with suction on a Buchner funnel, air dried thoroughly in the dark, and stored in the dark.

Preparation of 4-Nitrobenzenediazonium Ion Resin. In 24 ml. of hot 6N (1:1) hydrochloric acid solution, 5.52 grams (0.04 mole) of p-nitroaniline was dissolved, and the solution cooled to room temperature. Thirty-two grams of ice was added to the slurry of precipitated p-nitroaniline hydrochloride, and 2.84 grams (0.04 mole) of 97 per cent minimum assay sodium nitrite was added in one portion with vigorous stirring. The stirring was continued until almost all the precipitated salt had gone into solution, after which the solution was allowed to stand for 10 to 15 minutes in an ice bath. The solution was filtered, diluted to 100 ml. and added to 100 ml. (dry measure) of well-washed Amberlite IR-120(H) resin. The same procedure of stirring, washing, drying, and storing was followed.

2-Carboxy-4-Nitrobenzenediazonium Ion Resin. To 100 ml. of a solution containing 2.24 grams of potassium hydroxide was added approximately 1.4 grams of 5-nitroanthranilic acid (5-nitro-2-aminobenzoic acid). This gave a solution saturated with the potassium salt of the acid. It was found that sodium hydroxide was not satisfactory because it would not dissolve as much of the acid. Next, 0.6 grams of 97 per cent assay sodium nitrite was added to the solution. A small amount of ice was added to cool the solution which was then poured slowly with constant stirring into a beaker containing 60 grams of ice and

10 ml. of concentrated hydrochloric acid. After stirring 15 minutes in an ice bath, the slurry was filtered and added to 100 ml. of well-washed IR-120(H) resin. The same procedure of washing, drying and storing was again followed.

Preparation of 5-Nitroanthranilic Acid (5-Nitro-2-amino-benzoic acid). Sixty-five ml. of acetic anhydride and 34.3 grams of anthranilic acid were put in a 250 ml. round bottom flask and refluxed under a water-cooled condensor for  $\frac{1}{2}$  hour. The hot solution was poured in a thin stream into 2 liters of cold water with vigorous stirring. This mixture was cooled below  $10^{\circ}$  C with ice and the stirring was continued for some time to complete the slow precipitation of the acetyl derivative. The hard dense particles were allowed to settle out, and the less dense particles were decanted away and collected on a Buchner funnel. The residue on the filter was washed with three 100-ml. portions of 2N hydrochloric acid which had been cooled below  $10^{\circ}$  C with added ice, and then with three 100-ml. portions of ice-cold distilled water. After the residue had dried thoroughly at room temperature, it was dissolved in 115 ml. of cold concentrated sulfuric acid and cooled to 10 to  $20^{\circ}$  C.

The flask containing the completely dissolved acetyl derivative was placed in an ice-salt mixture, and 38 ml. of concentrated nitric acid was added dropwise with stirring at a rate that did not permit the temperature of the solution to rise above  $20^{\circ}$  C. After all the nitric acid had been added, the solution was stirred for 20 minutes outside of the cooling bath,

and poured slowly into 2 liters of water which was being vigorously stirred. Ice was added to bring the temperature below  $10^{\circ}\text{C}$  and the stirring continued for 20 to 30 minutes. The precipitate was filtered, washed with several portions of cold water, and then boiled for 15 minutes in 250 ml. of 6N (1:1) hydrochloric acid. The precipitate did not dissolve, but was hydrolyzed. After cooling to  $10^{\circ}\text{C}$  in an ice bath, the slurry was filtered and the residue washed with several portions of cold water.

The residue was then dissolved in boiling 95 per cent ethanol on a hotplate, two level teaspoons of decolorizing carbon were added, and the hot solution filtered. The residue on the filter paper was washed with a small volume of hot ethanol. The filtrate was brought to boiling on a hotplate and enough ethanol added to dissolve any precipitate. Cool water was then added to the boiling solution several ml. at a time, permitting the solution to again boil after each addition until a slight precipitate appeared. The solution was then set aside and permitted to come slowly to room temperature. The crystals were filtered on a Buchner funnel, washed with two 50-ml. portions of cool distilled water and dried.

Approximately 14.6 grams of 5-nitro-2-aminobenzoic acid were obtained. This was about 32 per cent of the theoretical yield. The product was light yellow to buff-colored needles which melted with decomposition at  $266^{\circ}$  to  $269^{\circ}\text{C}$ .



Diazonium Ions Prepared and Tested on Nuclear Sulfonic Acid IR-120(H) Resin. Included in this investigation were benzene-diazonium ion, 2-, 3-, and 4-nitrobenzenediazonium ions, 2,4-, 3,4-, and 3,5-dinitrobenzenediazonium ions, 2-methoxy-4-nitrobenzenediazonium ion, 2-methoxy-5-nitrobenzenediazonium ion, 2-chloro-5-nitrobenzenediazonium ion, 2-carboxy-4-nitrobenzenediazonium ion, 2- and 4-carboxybenzenediazonium ion, 4-chlorobenzenediazonium ion, 2,5-dichlorobenzenediazonium ion, 2-methoxy-5-chlorobenzenediazonium ion, 2-methoxybenzenediazonium ion, 4-arsenoxybenzenediazonium ion, 4-aminobenzenediazonium ion, 4,N,N-dimethylaminobenzenediazonium ion, 4-sulfonylbenzenediazonium ion, 4-sulfonamidebenzenediazonium ion, 3-quinoline-diazonium ion, 1- and 2-naphthalenediazonium ions, 4- and 5-nitronaphthalenediazonium ions, 4- and 5-carboxynaphthalenediazonium ions, 3- and 4'-nitrodiphenyldiazonium ions, 4'-chlorodiphenyldiazonium ion, and 4- $\alpha$ -pyridylbenzenediazonium ion.

#### Preparation of Spot-Test Papers

The general procedure was the same for all of the spot-test papers except that a 5 per cent solution of a soluble salt of a different metal was used for each one.

Whatman No. 42 filter paper, 7 cm. circles, was treated with 5 per cent solution, allowing about 3 ml. of solution for each circle. The papers were blotted free of excess solution between large sheets of qualitative filter paper and allowed to



dry in the air. The papers were then added to a saturated solution of p-arsanilic acid one at a time, allowing 10 ml. of solution for each paper. The papers were carefully washed five or six times in changes of distilled water and put, one at a time as rapidly as possible, into 100 ml. of solution containing 5 grams of 97 per cent minimum assay sodium nitrite and 2 ml. of concentrated hydrochloric acid. About 5 ml. of solution were allowed for each circle. After about three minutes the papers were carefully washed five or six times in distilled water, blotted free of water, air-dried in the dark, and stored in the dark.

The spot-test papers were prepared only with p-arsanilic acid. The salts used to anchor the p-arsanilic acid to the cellulose of the filter paper were aluminum nitrate, bismuth nitrate, cerium nitrate, lanthanum nitrate, stannic nitrate, thorium nitrate, yttrium nitrate and zirconyl chloride, all reagent grade.

The only ions that proved to be relatively effective for anchoring the p-arsanilic acid were stannic and zirconyl. The thorium ion was weak in this respect. Only the zirconyl-p-arsanilic acid papers have been studied further in this investigation because the stannic-p-arsanilic acid papers were a yellow color when dry.

### Objectives

The most desirable characteristics sought in a diazonium ion were rapid rates of coupling with phenols and aromatic

amines, stability in combination with the ion exchange resin, and ready release into solution from the resin by ion exchange. Also, diazonium ions were sought which would give intensely colored azo dyes. Some of the diazonium ions have a tendency to undergo hydrolysis to form slightly yellow color on standing in the mildly alkaline solution in which coupling reactions with phenols and aromatic amines are most rapid. The yellow color made it necessary to seek red colored dyes in preference to yellow or orange dyes. Red dyes that are moderately soluble under the conditions necessary for rapid coupling were sought for possible quantitative methods of analysis.

Many of the diazonium ion-resin combinations prepared were tested for stability by heating on a stainless steel spatula over a burner behind a safety shield. The concussion tests were performed by hitting the diazonium ion-resin combinations on an anvil with a hammer.

Only one of the investigated diazonium ion-resin combinations, that of p-arsanilic acid, showed any sign of explosiveness. When the resin dried out thoroughly, very mild explosions occurred spontaneously causing some of the resin beads to jump around. This was not due to any explosive tendency of the diazonium ion-resin combination, but to a solid diazonium salt that precipitated out when the diazonium solution was added to the acid form of the resin. None of the other diazonium ion-resin combinations showed any signs of explosiveness either on heating or concussion.

One batch of 4-nitrobenzenediazonium ion-resin combination was divided into two parts. One part bottled, stoppered, and stored moist in the dark, and the other part was dried before storing. The reactivity of each with resorcinol was tested when first stored and again after a month of storage. The moist combination had formed a gas pressure in the bottle, which was probably due to nitrogen. The moist combination smelled strongly of nitrobenzene, gave a brown color to distilled water, and was much less reactive with resorcinol when released from the resin with potassium chloride. The dry combination had only a faint odor of nitro-benzene, and was apparently as reactive with resorcinol as when it was first prepared. Strong light caused relatively rapid deterioration of the diazonium ions even on the dry resin.

The zirconyl-p-arsanilic acid diazonium ion spot-test papers underwent a gradual deterioration with time, but still gave a faint reaction after five months.

It has been found in general that the reactivity of a diazonium ion in the coupling reaction and its storage stability on a resin are directly proportional to the cationicity of the diazonium ion. Diazonium ions are generally regarded as cationoid rather than cationic, but they become true cations with the substitution of negative groups on the aromatic ring (Venkataraman, 6, p. 413). The nitro group is outstanding for this purpose, as shown by coupling reaction rate studies, and it is a chromophore in addition. Chlorine, carboxyl, and sulfonic

acid groups are less effective, the latter two favoring the formation of difficultly-soluble zwitter ions. Acid substituent groups, however, impart solubility in basic solution to the azo dye.

It was found that substituents other than the carboxyl groups adjacent to the diazonium group undergo rapid replacement by a hydroxyl, with formation of the non-reactive diazo-oxides, when a negative substituent is in the 4-position on the benzene ring. This does not occur when the negative group is on the 5-position.

Ring systems other than benzene did not produce very satisfactory diazonium ions. Those with naphthalene and diphenyl ring systems were little, if any, better color-formers than the corresponding benzene derivatives. Also, the stability, storage on ion exchange resin, and rate of coupling apparently were not as good.

Of those prepared, only the 2-carboxy-4-nitrobenzenediazonium ion, the 2,5-dichlorobenzene diazonium ion and the 4-nitrobenzenediazonium ion seemed satisfactory for use as resin-stabilized reagents. They were stable over a period of six months to a year with very little decomposition when stored dry in the dark at room temperature. Other diazonium ions proved to be stable, but generally for shorter periods of time. The 4-nitrobenzenediazonium ion was a better color-former and more effective in coupling than the 2-carboxy-4-nitrobenzenediazonium ion; however, the dyes of the latter had better

solubility in the moderately alkaline solutions used. Both formed slightly yellowish colors in alkaline solution, which became colorless when the solution was made acid. The 2,5-dichlorobenzenediazonium ion was not quite as good a color-former as the 4-nitrobenzenediazonium, but it does not form a blank with a noticeable yellow color in alkaline solution.

### Qualitative Investigations

Tests with the 3 diazonium ions that seemed to have the most desirable characteristics were run on 30 phenols and aromatic amines. Special attention was taken to notice the relative intensity of the color, the color of dye produced, and the pH at which it was produced as shown in Tables 1, 2, and 3.

The solutions for the qualitative tests given in Tables 1, 2, and 3 were prepared by pipeting 1 ml. of a 0.1 per cent solution, or a saturated solution if the compound is not very soluble, of an aromatic amine or phenol into a 50 ml. beaker. To this was added 5 ml. of buffer solution. The solution was then stirred and 1 ml. of the diazonium ion solution was added.

The diazonium ion solution was prepared by mixing  $\frac{1}{4}$  teaspoon of potassium chloride and one teaspoon of the diazonium ion-resin combination with 50 ml. of water.

The measured pH values were those obtained after the strongly acid diazonium ion solution was added; therefore, the solutions were all slightly more acid than the listed pH of the buffers.



Table 1. Colors of the azo dyes formed by 2,5-dichlorobenzene-diazonium ion with various aromatic amines and phenols at different pH values.

Compound	pH of Solution				
	1.8	4.8	6.8	8.8	12.5
Phenol	col.	ft.y	ft.o	y	y
o-Cresol	col.	ft.y	y	y-o	y-o
p-Cresol	col.	col.	lt.y	y	ft.o
Resorcinol	ft.y	y-o	o	o	o
Catechol	ft.y	y-b	y-b	y-b	ft.o
Phloroglucinol	o	r-o	r-o	r-o	o
Salicylic acid	col.	col.	col.	lt.o	col.
Aniline	col.	lt.y	lt.y	lt.y	col.
N-methylaniline	lt.y	lt.y	lt.y	lt.y	col.
N,N-dimethylaniline	col.	o	o	o	col.
Diphenylamine	ft.y	lt.y	lt.y	lt.y	col.
m-Phenylenediamine	y-o	o	o	o	lt.o
Benzidine	col.	y-g	y-g	y-g	ft.o
8-Hydroxyquinoline	col.	lt.o	o	r-b	r-o
$\alpha$ -naphthol	y	o	o-b	b	lt.r
$\beta$ -naphthol	lt.r-o	o	o	o	lt.o
1-Naphthol-4-sulfonic acid	ft.o	o	o	o	ft.r
2-Naphthol-6-sulfonic acid	col.	y-o	o	o	ft.o
2-Naphthol-3,6-disulfonic acid	col.	lt.o	o	r-o	ft.r
3-Hydroxy-2-naphthoic acid	col.	ft.o	lt.o	o	lt.o
$\alpha$ -naphthylamine	o-b	b	r-o	r-o	lt.r-o
$\beta$ -naphthylamine	o	o	o	o	ft.r
Naphthoic acid	y-o	y-o	y-o	y-o	col.
1-Amino-2-naphthol-4-sulfonic acid	lt.y-o	lt.y-o	lt.o	lt.o	ft.y
1-Amino-8-naphthol-3,6-disulfonic acid	lt.r	r-v	r-v	r-v	v
2-Amino-1-naphthalenesulfonic acid	ft.y-o	o	y-o	lt.y-o	col.
2-Amino-8-naphthol-6-sulfonic acid	lt.r	r	r	r-v	r-v
1-Tyrosine	col.	col.	col.	y	lt.r-o
dl-Histidine	col.	col.	col.	o	y-o
dl-Tryptophane	lt.y	lt.y	lt.y	lt.y	col.
Water	col.	col.	col.	col.	col.

Legend of colors.

col., colorless	b, brown	r, red
ft., faint	g, green	v, violet
lt., light	o, orange	y, yellow



Table 2. Colors of the azo dyes formed by 4-nitrobenzenediazonium ion with various aromatic amines and phenols at different pH values.

Compound	pH of Solution				
	1.8	4.8	6.8	8.8	12.5
Phenol	col.	lt.y	y	o	o
o-Cresol	col.	y	y-o	r-b	r-o
p-Cresol	col.	col.	lt.y	y-o	y
Resorcinol	lt.y-o	o	o	o-b	r-b
Catechol	ft.y	o	o	b	y-o
Phloroglucinol	lt.y-o	o	o	o	o
Salicylic acid	col.	col.	lt.y	y-o	y
Aniline	lt.y	o	o	o	y
N-methylaniline	y-o	o	o	o	y
N,N-dimethylaniline	lt.r	r	r	r	y
Diphenylamine	ft.o	ft.o	lt.y	lt.y	y
m-Phenylenediamine	y-o	r-o	b	b	y-o
Benzidine	ft.y	lt.y	lt.y	lt.y	y
8-Hydroxyquinoline	ft.y	r-o	r-o	b	y
$\alpha$ -naphthol	y-o	r-o	r-o	b	y-b
$\beta$ -naphthol	col.	lt.o	o	o	y-o
1-Naphthol-r-sulfonic acid	ft.r	r-o	o	o	y
2-Naphthol-y-sulfonic acid	col.	y-o	o	r-o	y
2-Naphthol-3,6-disulfonic acid	col.	lt.o	o	r-o	y
3-Hydroxy-2-naphthoic acid	col.	ft.r-o	lt.o	r-o	y-o
$\alpha$ -naphthylamine	r-v	v	v	v	y
$\beta$ -naphthylamine	r-v	r-v	r-v	r-v	y
Naphthoic acid	lt.r	r-o	r-o	r-o	y
1-Amino-2-naphthol-4-sulfonic acid	lt.y-o	lt.y	y-o	y-o	y
1-Amino-8-naphthol-3,6-disulfonic acid	lt.v	v	v	v	v
2-Amino-1-naphthalenesulfonic acid	lt.r	lt.r	lt.r-o	lt.o	y
2-Amino-6-naphthol-6-sulfonic acid	lt.v	r-v	b	b	v-b
l-Tyrosine	col.	col.	y	lt.o	y
dl-Histidine	col.	col.	lt.y	y-o	y-o
dl-Tryptophane	col.	lt.y	lt.y	y	y
Water	col.	col.	lt.y	lt.y	lt.y

Legend of colors.

col., colorless	b, brown	r, red
ft., faint	g, green	v, violet
lt., light	o, orange	y, yellow

Table 3. Colors of the azo dyes formed by 2-carboxy-4-nitro-benzenediazonium ion with various aromatic amines and phenols at different pH values.

Compound	pH of Solution				
	1.8	4.8	6.8	8.8	12.5
Phenol	col.	col.	col.	lt.o	col.
o-Cresol	col.	col.	col.	r-o	ft.r
p-Cresol	col.	col.	col.	ft.o	ft.y
Resorcinol	col.	ft.y	lt.y	y-o	y-o
Catechol	col.	col.	ft.y	ft.y	lt.o
Phloroglucinol	col.	ft.o	y-o	y-o	y-o
Salicylic acid	col.	col.	col.	col.	ft.y
Aniline	col.	col.	ft.y	lt.y	ft.y
N-methylaniline	col.	ft.y-o	lt.y	lt.y	ft.y
N,N-dimethylaniline	col.	ft.r	ft.o	ft.y	ft.y
Diphenylamine	col.	col.	ft.y	ft.y	ft.y
m-Phenylenediamine	col.	o	o	r	ft.o
Benzidine	col.	ft.b	ft.y	lt.y	y
8-Hydroxyquinoline	col.	col.	y-o	y-o	v
$\alpha$ -naphthol	col.	lt.o	lt.r-o	lt.r-o	r-b
$\beta$ -naphthol	col.	col.	ft.r	lt.r	ft.o
1-Naphthol-r-sulfonic acid	col.	col.	ft.o	lt.r-o	col.
2-Naphthol-y-sulfonic acid	col.	col.	ft.o	lt.y-o	col.
2-Naphthol-3,6-disulfonic acid	col.	col.	col.	ft.r-o	col.
3-Hydroxy-2-naphthoic acid	col.	col.	ft.y	lt.o	ft.o
$\alpha$ -naphthylamine	ft.v	v	v	r-b	col.
$\beta$ -naphthylamine	col.	ft.r	ft.r	lt.r	ft.y
Naphthoic acid	col.	col.	ft.y	ft.y	ft.y
1-Amino-2-naphthol-4-sulfonic acid	col.	col.	ft.y	lt.y	lt.y
1-Amino-8-naphthol-3,6-disulfonic acid	ft.v	r-v	r-v	r-v	v
2-Amino-1-naphthalenesulfonic acid	col.	col.	ft.y	ft.y	ft.y
2-Amino-8-naphthol-6-sulfonic acid	col.	r-v	r	r	r-b
l-Tyrosine	col.	col.	ft.y	ft.r	ft.y
dl-Histidine	col.	col.	ft.y	lt.r	ft.y
dl-Tryptophane	col.	col.	ft.y	ft.y	col.
Water	col.	col.	lt.y	ft.y	ft.y

Legend of colors.

col., colorless	b, brown	r, red
ft., faint	g, green	v, violet
lt., light	o, orange	y, yellow

Table 4. Colors of the azo dyes formed p-arsonilic acid-zirconyl chloride spot-test papers with various aromatic amines and phenols at different pH values.

Compound	Solutions			
	:	:	:	:
	(1:1):	(1:1):	(1:1):	undiluted
	pH(5)	pH(9)	NaAc	solution
Phenol	col.	y	lt.y	col.
o-Cresol	col.	o	y	col.
p-Cresol	col.	o-b	y	col.
Resorcinol	y-o	y-o	y-o	y-o
Catechol	lt.o	lt.o	lt.y-o	ft.o
Phloroglucinol	y-o	y-o	y	y-o
Salicylic acid	col.	ft.y-o	col.	col.
Aniline	y	lt.y	ft.y	lt.y
N-methylaniline	lt.o	lt.y-o	lt.o	lt.y-o
N,N-dimethylaniline	o	lt.o	y-o	o
Dephenylamine	col.	lt.y-o	col.	ft.y-o
m-Phenylenediamine	y-o	y-o	y-o	y-o
Benzidine	lt.y-g	lt.y-o	ft.y	ft.y-g
8-Hydroxyquinoline	lt.o	r-o	o	lt.o
$\alpha$ -naphthol	o	r	o	o
$\beta$ -naphthol	lt.o	y-o	lt.o	ft.o
1-Naphthol-4-sulfonic acid	lt.r-o	lt.r-o	r-o	ft.o
2-Naphthol-6-sulfonic acid	lt.y-o	o	lt.o	col.
2-Naphthol-3,6-disulfonic acid	lt.r-o	lt.r-o	lt.r-o	ft.o
3-Hydroxy-2-naphthoic acid	lt.r	lt.r-o	lt.r-o	lt.r
$\alpha$ -naphthylamine	r	o	r-o	r
$\beta$ -naphthylamine	lt.o	lt.y-o	lt.o	lt.o
Naphthoic acid	lt.o	ft.o	ft.o	lt.r-o
1-Amino-2-naphthol-4-sulfonic acid	lt.y-o	lt.y-o	lt.y-o	y-b
1-Amino-8-naphthol-3,6-disulfonic acid	r-v	r-v	r	r-v
2-Amino-1-naphthalenesulfonic acid	y-o	ft.y	lt.y-o	lt.y-o
2-Amino-8-naphthol-6-sulfonic acid	r-o	r-b	r-b	lt.r-o
Water	col.	col.	col.	col.

Legend of colors.

col., colorless	b, brown	r, red
ft., faint	g, green	v, violet
lt., light	o, orange	y, yellow

The solutions for application to the spot-test papers were prepared by mixing 5 ml. of buffer with 5 ml. of 0.1 per cent, or saturated, phenol or aromatic amine solution and mixing. One drop of this solution was applied to the spot-test paper.

The stannic nitrate paper gave colors ranging from yellow-orange to red-orange with phenol, aniline, resorcinol, beta-naphthylamine, and m-phenylenediamine. However, it had a yellow color before use which would make detection of yellow-colored coupling products difficult.

#### Quantitative Investigations

The possibility of using the diazonium ion in quantitative work was studied by first running the optical density versus wavelength curve for some of the phenolic compounds to determine the wavelength of the maximum optical density. The results are listed in Table 5.

Table 5. Maximum optical density of benzenediazonium ions when coupled with phenol, o-cresol, or p-cresol.

Benzenediazonium ion	Coupled to	$\lambda$ of O.D. max.
2-carboxy-4-nitro-	o-cresol	500 $m\mu$
" "	p-cresol	524 $m\mu$
2,5-dichloro	phenol	444 $m\mu$
"	o-cresol	456 $m\mu$
"	mixture phenol, o-cresol	452 $m\mu$

The 2-carboxy-4-nitrobenzenediazonium ion-phenol coupling did not give a distinct maximum in the visible range examined, but only the shallow peak due to the diazonium ion itself. The 2,5-dichlorobenzenediazonium ion forms a turbid solution with the p-cresol.

The directions for preparation of standard solutions of phenol and the cresols were found in standard methods for the examination of water and sewage (5), p. 216.

Quantitative determinations of absorbance (optical density) versus the concentration were run by pipetting 10 ml. of phenol or cresol solution, 2 ml. of 1 M sodium carbonate solution, and 1 ml. of diazonium ion solution, prepared as previously described, into a 50 ml. beaker and mixing thoroughly. After about 30 minutes the sample was put into the absorption cell and the absorbance taken at the proper wavelength on the Beckman Model DU spectrophotometer.

A study of the effect that varying the amount of diazonium ion had upon the absorbance revealed that the absorbance was related to the volume of diazonium ion solution used, but that a small error in measuring the volume had little effect upon the reproducibility of the results.

Using 2,5-dichlorobenzenediazonium ion, the relationships of absorbance versus concentration were determined for phenol and o-cresol. These relationships appeared to be practically linear in the range 0.1 parts per million to 10 parts per million, but they had slightly different slopes. The same

relationship was determined for a mixture of phenol and o-cresol and found to be practically linear also. The molar extinction coefficients were  $1.29 \times 10^4$  for phenol,  $1.84 \times 10^4$  for o-cresol, and, using 101 for the average molecular weight,  $1.30 \times 10^4$  for a mixture of phenol and o-cresol. With distilled water in the second cell, there was a 0.1 intercept on the absorbance axis for the mixture of phenol and o-cresol, indicating a very faintly colored blank. The formula for the molar absorptivity is:

$$\epsilon = \frac{\text{absorbance}}{\text{concentration} \times \text{cell length}} \times \text{molecular weight.}$$

The concentration is expressed in parts per thousand and the cell length is in centimeters.

Quantitative tests were run on o-cresol and p-cresol with 2-carboxy-4-nitrobenzenediazonium ion. In the concentration range 0.2 to 10 parts per million, o-cresol produced a practically linear relationship; however, p-cresol did not have sufficient absorbance to be investigated in this range. In the concentration range 20 to 1000 parts per million, p-cresol produced an absorbance versus concentration relationship which was not quite linear particularly at the lower end. It was also noticed that at extremely high concentrations of the phenolic compound, 1 ml. of the diazonium ion solution did not give a linear relationship because insufficient diazonium ion was present. Better results were obtained when 2 ml. of diazonium ion were added to these solutions. The molar extinction coefficients were  $3.6 \times 10^3$  for o-cresol using 1 ml. of diazonium ion, and  $5.4 \times 10^1$  for p-cresol using 2 ml. of



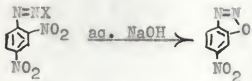
diazonium ion. These curves were all found to be reproducible.

### DISCUSSION

Venkataraman (6), p. 413, stated that in general, diazonium salts of negatively substituted amines, such as the nitroanilines nitrochloroanilines, and the aniline sulfonic acids couple more rapidly due to the inductive and resonance effects of the nuclear substituents. The nitro is especially effective on account of the positive polarization of the nitrogen atom, which withdraws electrons from the ring and increases the positive charge on the diazonium ion. When the nitro group is in the o- or p-position, the resonance effect further enhances the positive charge on the diazonium group. The diazonium group may then be regarded as not merely cationoid in character, but as a definite and powerful cation. Nuclear halogen atoms, owing to their strongly electronegative character, have an inductive effect in the same sense, but since any resonance effect functions in the opposite direction the influence of halogen atoms on coupling is of a minor order in comparison with nitro groups.

The work of this investigation agreed with the information given above in most respects. The three diazonium ions with the most desirable characteristics were nitro and chloro substituted. Their stability and rapid coupling rates can be attributed to the above factors. It was found that the ortho nitro substituted rings gave a yellow color in aqueous solution. With

two nitro groups substituted on the ring, one being in the ortho position, the yellow color appeared more quickly and became more intense. This color is probably due to hydrolysis and diazo-oxide formation as described by Saunders (3), p. 117. The chlorine substituted diazonium ions do not show as great a tendency for exchange and the carboxyl group is the only one that will stay on the ortho position when a negative group is in the para position. For this reason none of the ortho nitro compounds were satisfactory. The reaction of 2,4-dinitrobenzenediazonium ion is:



A comparison of Tables 1, 2, and 3 reveals that the coupling products of 4-nitrobenzenediazonium ion were generally nearer to red than those of the other diazonium ions. This was one of the characteristics being sought. The colors of the coupling products of 2,5-dichlorobenzenediazonium ion were nearly as satisfactory, with those of 2-carboxy-4-nitrobenzenediazonium ion being least satisfactory.

One advantage of 2,5-dichlorobenzenediazonium ion over 4-nitrobenzenediazonium ion was its ability to give a colorless blank in either acid, neutral or alkaline solution, where the 4-nitrobenzenediazonium ion and the 2-carboxy-4-nitrobenzenediazonium ion gave slightly yellow blanks in alkaline solution. The reaction of the 4-nitro- and 2-carboxy-4-nitrobenzenediazonium

ions to form yellow solutions was undoubtedly the replacement of the diazo group by a hydroxyl group to produce a phenol as described by Saunders (3), p. 302. The equations for the reaction are:



To check the possibility that the color of the solution was due to p-nitrophenol, acid and alkaline solutions of p-nitrophenol were prepared. It was found to be colorless in acid solution and yellow in alkaline solution, and very similar to the hour old solutions of p-nitrobenzenediazonium ion. It was found that 2,4-dichlorophenol is colorless in either acid or alkaline solution, and so it seems that 2,5-dichlorophenol would probably be colorless under the same conditions. The 2,5-dichlorophenol was not readily available to test this conclusion.

The order of intensity of color was in agreement with previous work as quoted by Venkataraman (6), p. 323. The nitro group functions as a chromophore to give color and make the 4-nitrobenzenediazonium ion a strong color former. This same fact is responsible for the yellow blank obtained in alkaline solution. The chlorine atom is not a chromophore, but is a weakly auxochromic group, and for this reason the dichloro compound was a good color-former. It still was not as good as the 4-nitro compound. Because the chlorine atom does lack

chromophoric qualities, the 2,5-dichlorobenzenediazonium ion is capable of giving a colorless blank.

A further study of Tables 1, 2, and 3 has revealed that many of the phenols and aromatic amines behaved differently at different pH values, and this behavior can be used to determine which amine or phenol. For instance, if a solution was suspected of containing either phenol, o-cresol or p-cresol, any one of the three gives a colorless mixture with either 2,5-dichloro- or 4-nitrobenzenediazonium ion in water at a pH of 1.8. At a pH of 4.8 only the p-cresol is colorless. If a color is obtained at a pH of 4.8, eliminating p-cresol, the solutions can be made again at a pH of 6.8. With 2,5-dichlorobenzenediazonium ion the phenol solution is a faint orange color, but the o-cresol is yellow. A double check can be made by using the 4-nitrobenzenediazonium ion which gives a slight reversal of the colors--the phenol is yellow and the o-cresol is yellow-orange. If desired a triple check can be made by using another diazonium ion such as 2-carboxy-4-nitrobenzenediazonium ion.

Examination of Table 4 has shown possibilities for the use of the zirconyl chloride, p-arsonilic acid spot-test papers in qualitative analysis. The various amines and phenols gave quite different colors at different pH values, as a general rule. This is true of phenol which changes from faint yellow at a pH of 5 to yellow at a pH of 9, for o-cresol which changes from faint yellow at a pH of 5 to orange at a pH of 9, or for p-cresol

which changes from colorless at a pH of 5 to orange-brown at a pH of 9.

The information in Table 5 and the explanation following it show that the polyanion stabilized diazonium cations could also be used in the standard methods of quantitative colorimetric analysis (4), (5), (7), with only modifications in the procedures.

### CONCLUSION

Of 33 ion exchange resin-stabilized diazonium ions investigated, the three exhibiting outstanding possibilities were 2,5-dichlorobenzenediazonium ion, 4-nitrobenzenediazonium ion, and 2-carboxy-4-nitrobenzenediazonium ion. Of eight cellulose anchored diazonium ion spot-test papers investigated, the one having excellent characteristics was the zirconyl chloride-p-arsonilic acid paper, while the stannic nitrate-p-arsonilic acid paper had good characteristics.

Diazonium ions dispersed on nuclear sulfonic acid ion exchange resin or by salt formation to filter paper are quite stable and can be safely stored in a dry state.

Certain polyanion-stabilized diazonium ions are stable for extended periods of time, form characteristic colors when coupled with specific phenols or aromatic amines at various pH values, and produce linear or nearly linear absorbance versus concentration relationships for colorimetric or spectrophotometric analysis. Other polyanion stabilized diazonium ions are stable

for short to moderately long periods of time and might be used advantageously for analytical reagents, also.



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THE USE OF POLYANION-STABILIZED DIAZONIUM  
CATIONS AS ANALYTICAL REAGENTS

by

VERNON EUGENE CATES

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Diazonium ions can be stabilized by dispersion upon cation exchange resin, and released again for use by exchange with potassium ion in solution. Through salt formation with zirconyl ion, p-arsonilic acid can be chemically anchored to filter paper and diazotized to form a stable diazonium ion spot-test paper.

The purpose of this investigation has been to study these stabilized diazonium compounds and their possible applications in developing more convenient analytical procedures.

Thirty-three ion exchange resin-diazonium ion combinations and eight cellulose anchored diazonium ion spot-test papers were prepared and investigated. Those showing outstanding characteristics of storage stability, rapid coupling reaction, coupling products near red in color, solubility of the dye produced, and colorless blanks were investigated further.

Qualitative tests were made by reacting the diazonium ions having the most desirable characteristics with 30 aromatic amine and hydroxy compounds at pH values 1.8, 4.8, 6.8, 8.8, and 12.5.

The wavelength of maximum absorbance was determined for five combinations of diazonium ions with phenol, o-cresol, and p-cresol. The relationships of absorbance versus concentration were determined for four combinations and the reproducibility of results was checked.

Three diazonium ion-resin combinations exhibited outstanding properties. The one giving a colorless blank was 2,5-dichloro-benzenediazonium ion. The 4-nitrobenzenediazonium ion coupled

more rapidly and gave colors nearer to red, but it gave a blank with a slight yellow color. Greater solubility of the coupling products was imparted to the dyes formed with 2-carboxy-4-nitro-benzenediazonium ion, which did not couple as rapidly nor produce as satisfactory colors as the other two diazonium ions. All three were stable over a long period of time when the resin was stored dry and in the dark. The diazonium ion-resin combinations listed had excellent properties for quantitative as well as qualitative applications. Some procedures have previously been developed for quantitative work to which these diazonium ions can be adapted.

The spot-test papers of stannic and zirconyl salts showed ability to anchor p-arsonilic acid to filter paper. The diazotized papers thus prepared produced desirable colors with aromatic amine and hydroxy compounds. The zirconyl papers were much better because they were nearly colorless whereas the stannic papers were distinctly yellow. The zirconyl papers exhibited excellent properties for qualitative tests.

