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This ~~memorandum~~ report reviews the analytical chemistry of hydrazine and its methyl derivatives. The purpose is to develop chemical approaches for synthesis of hydrazine vapor specific coatings for chemical microsensors. ~~It is divided into six sections.~~ Section 1 discusses basic hydrazine chemistry relevant to the analytical reactions presented in subsequent sections and to the coating requirements for chemical microsensors. Sections 2, 3, 4 and 5 discuss specific analytical hydrazine reactions which have been classified as aldehyde or ketone condensations, aromatic nucleophilic displacements, organic compound or metal ion reductions and organic dye interactions respectively. Section 6 presents chemical approaches suggested for microsensor coatings. Originator-supplied Keywords Included;

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CONTENTS

REVIEW OF SPECIFIC CHEMICAL INTERACTIONS FOR HYDRAZINE ANALYSIS AND PROPOSED ADAPTATION FOR MICROSENSOR CHEMICAL DETECTION

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INTRODUCTION

Hydrazine and its derivatives, while necessary for hypergolic fuel applications, are hazardous as toxic vapors at the ppm level and as explosive air mixtures at higher concentrations. Since the early 1960's much effort has been directed toward detection and monitoring of hydrazines in ambient air. Commercial instruments and devices for this purpose have been developed and recently reviewed[1]. The devices are based on electrochemical, chemiluminescent, infrared spectroscopic and colorimetric methods. Most of these devices have substantial requirements with regard to high cost and large physical size. The purpose of this report is to explore a microsensor approach to hydrazine detection based on its known molecular chemistry. The advantages of this approach are a large reduction in device size (approaching the order of a few cubic centimeters) and reduction in cost (approaching a disposable item). Microsensors will probably not compete with larger devices where ultimate sensivity and specificity are required, but will find application where large numbers of units are required such as monitoring networks in compartmental structures and as personal dosimeters.

The microsensor approach involves devices consisting of two primary components: a physical probe and a coating. The physical probe detects changes in the coating's properties induced by interaction with a particular vapor and converts it into an electronic signal. Probes currently being investigated as part of a Naval Research Laboratory microsensor program are a surface acoustic wave (SAW) device, an optical wave guide and a chemiresistor. The SAW device measures velocity of a Raleigh surface wave on a piezoelectric substrate and is very sensitive to gravimetric and mechanical property changes of an applied coating. The optical wave guide measures transmission attenuation of internally reflected light passed through an optical

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fiber or capillary and is very sensitive to optical property changes of an applied coating. The chemiresistor measures electrical resistivity of thin semiconducting organic coatings on a microinterdigital electrode array and is very sensitive to electrical property changes. The physics of these probes have been described elsewhere[2]. The coating is a thin uniform deposition of an organic substance onto the probe surface. It is ideally designed to have a specific chemical receptivity to a particular vapor whose interaction coincidentally produces a property change that is easily registered by the probe. In addition to meeting the requirements of the probe's sensing property and the particular vapor's chemistry, the coating must be applied in a very thin, uniform and reproducible manner (i.e. quantity of material deposited, uniformity in thickness and morphology). Two techniques of meeting the coating application requirements are spin coating of soluble polymeric materials and Langmuir-Blodgett transfer of mono and multimolecular layers of appropriately structured organic compounds.

The specific purpose of this report is to examine and briefly review hydrazine analytical chemistry that may be adaptable to a coating for a solid-state microsensor. Many of the reactions, which are reviewed, were studied in a uniphase solution. The microsensor application is a heterogeneous gas-solid system. Extrapolation implies similar chemistry will occur heterogeneously. However, while many of the solution hydrazine reactions are analytically quantitative, this requirement is not necessary for the microsensor, which would be empirically calibrated in controlled atmospheres. Some reactions are reversible, while others are not. For the purpose of microsensor development, the former are regarded as candidates for detectors while the latter for dosimeters.

This report is organized into six technical sections. The first section discusses some fundamental characteristics of hydrazine chemistry that are useful in understanding some of the analytical reactions presented in later sections. An excellent and exhaustive monograph on hydrazine and its derivatives has very recently appeared and is very useful for indepth study[3]. The analytical reactions in the next four sections have been classified according to type, which include aldehyde and ketone condensations, organic compound and metal ion reductions, nitro-activated aromatic nucleophilic displacements and organic dye electrical responses. Within each section the specific reactions are presented in the chronological order that they appear in the literature. A final section will conclude with an assessment of systems that may be adaptable for a sensor coating.

1. HYDRAZINE CHEMICAL CHARACTERISTICS.

The chemistry of a successful hydrazine specific coating will be dependent on specific interactions that take advantage of attractive forces than exist between hydrazine (or a derivative) and the coatings' composition. The interactions, which vary in strength and specificity, take the form of a physical absorption, a complex formation, a covalent bond forming reaction or a redox chemical reaction. These interactions relate to the hydrazine structure and will be discussed in the context of coating specificity development.

The physical absorption interaction is the weakest, least specific, but most reversible. Qualitatively, this effect may be enhanced by matching the polarity of the coating with the vapor. Such an empirical approach has been employed in the detection of unsymmetrical dimethyl hydrazine by copolymer coatings of butadiene-acrylonitrile and butadiene-styrene on a piezoelectric crystal sensor[4]. Quantitatively, the physical absorption is usually described on the macroscopic level by thermodynamic parameters for dissolution compatibility or absorption chromatography. The simplest example is the Scatchard-Hildebrand solubility parameter for regular solutions[5]. While limited by the regular solution model from which it is derived, this parameter can serve as a guide in the formulation of a coating. For detection of vapors in air, this absorption interaction is exploited to achieve a maximum partitioning between the coating and air. With the solubility parameter approach, the values for the vapor and coating are matched as closely as possible. For hydrazine, monomethyl hydrazine and unsymmetrical dimethyl hydrazine the solubility parameters are 17.8, 13.1 and 10.1 $cal^{.5}/cm^{1.5}$ respectively[6]. For the above mentioned UDMH experiment, the detection sensitivity range was 2 to 115 ppm but the selective coating response does not follow that predicted by the solubility parameters (Table 1).

Table 1

Coated Piezoelectric Crystal Detection Response to Unsymmetrical Dimethyl Hydrazine[4]

Coating	δ $(cal/cm^3)^{.5}$	Response to 100 ppm UDMH (Hz)	Response/Polymer wt. x 10^{-4}
$A_{.22}B_{.78}$	8.7	14	8.85
$A_{.45}B_{.55}$	10.3	12	7.47
$S_{.24}B_{.76}$	8.2	20	21.1
$S_{.48}B_{.52}$	8.8	22	20.7

A Acrylonitrile; B Butadiene; S Styrene; Solubility parameter data from reference 5.

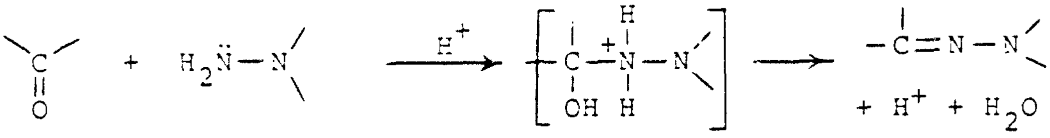
The strength of the solubility parameter approach is also its weakness. Predictions may be made from tabulated data of individual system components; however, the regular solution model does not allow for exothermic heats of mixing from intercomponent specific interactions (e.g. hydrogen bonding). More sophisticated theories accomodate exothermic heats of mixing, but require data to be taken on the specific system[7]. The objective in discussing the above example is to demonstrate that good sensitivities are obtainable using the physical absorption interaction. It is also evident that use of a physical absorption optimized coating component as a binder, overcoating or protective membrane to concentrate vapor could enhance the optical or electrical response of another reactive component within the coating.

The more specific interactions, involving the capacity of hydrazines to act as bases, nucleophiles or reducing agents, are functional group centered and are dependent on the uniqueness of the hydrazines' molecular chemistry. From their structure, hydrazines may be regarded as diamines with a unique capability for undergoing oxidation. As a base, hydrazine is stronger than water but weaker than ammonia. The effect of mono and diakyl substitution is to slightly decrease the base strength by a fraction of a pK unit. This consideration could be of discriminating importance for interactions where proton transfer is involved such as with acidic dyes or in the formation of hydrogen bonded complexes. Hydrazines may also act as Lewis bases and form coordination complexes with transition metal ions or charge transfer complexes with organic or inorganic Lewis acids. If charge transfer is complete in these complexes, the result may be oxidation of the hydrazine and reduction of the Lewis acid component. If the Lewis acid is stable toward reduction, a nucleophilic addition or substitution may be the result. In contrast to basisity, nucleo-philicity increases with alkyl substitution. The important consequences for chemical detection are the reversibility of the complex formation and the property change that accompanies complex or reaction product formation. The redox and nucleophilic reactions are mostly irreversible, and detection schemes based on them would find application as dosimeters. Analytical reactions based on this irreversible chemistry include aldehyde and ketone condensations, organic compound and metal ion reductions and nucleophilic aromatic displacements. These reactions will be reviewed in the following three sections. If the complex formation involves partial or reversible transfer of protons or electrons and a nucleophilic reaction does not occur, the interaction is reversible and forms the basis for a sensor with a vapor concentration dependent response. Semiconducting organic dyes with electrical and optical responses to hydrazine vapors appear to have these reversible characteristics and will be reviewed in Section 5.

Finally, to develop a coating that has high molecular specificity for particular vapor, it is necessary to employ a chemically specific structure as the coating itself or to incorporate it into a host coating either by occlusion or covalent bonding. Examples of each would be a sublimed phthalocyanine film as a molecular coating, benzaldehyde occluded in polyisoprene as an occluded polymer coating and polynitrostyrene as a functionalized polymer coating. A further requirement is the vapor-coating molecular interaction must be transitioned into a macroscopic coating property change (e.g. mechanical, gravimetric, electrical, optical, etc.) This coating property change may be functional group centered as in the conductivity change caused by reduction of a phthalocyanine ring or a color change from condensation with an aldehyde or may be coating matrix centered as in an optical light scattering change of a liquid crystal matrix caused by reaction of occluded small molecules with hydrazine. A cholesteryl chloroformate liquid crystal coating has been found to have an 8 ppm level sensitivity to hydrazine and and 1,1-dimethylhydrazine as detected by a green to red color change[7a]. Approaches by which hydrazine reactive functionalities might be incorporated into sensitive coatings will be presented in Section 6.

2. ALDEHYDE AND KETONE CONDENSATIONS.

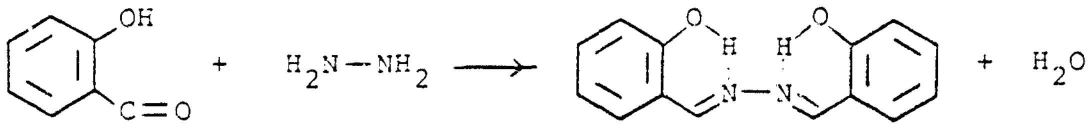
The condensation of a hydrazine with an aldehyde or ketone involves the nucleophilic addition of the nitrogen base, which is frequently acid catalyzed by protonation of the carbonyl, followed by elimination of water to yield the hydrazone or azine product depending on whether one or both of the nitrogens react.



The reaction requires that the aldehyde or ketone substituent be aromatic and is usually conducted in aqueous or alcoholic medium.

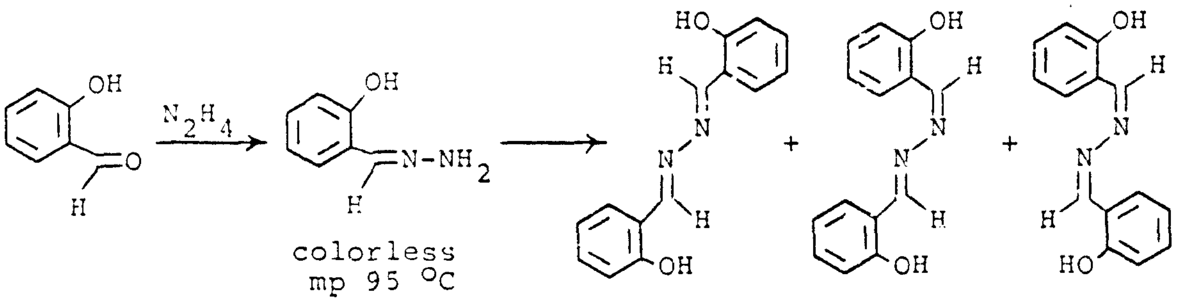
1. Salicyaldehyde.

As a quantitative analytical reagent for hydrazine, benzaldehyde preceded salicyaldehyde but had disadvantages in that benzaldehyde is not very water soluble and its occlusion in the precipitated benzaldazine product interferred with the gravimetric analysis[8]. The more water soluble salicladehyde yields a water-insoluble condensation product which allows hydrazine quantities as low as 0.1 μg to be determined by a turbidity observation[8]. The low aqueous solubility of the salicyaldazine product was attributed to formation of an "inner complex" salt.



bright yellow

Thirty years later, very careful analytical chemistry showed the above chemistry to be oversimplified. The intermediate salicylaldazone and three isomeric salicyaldazines were isolated and characterized[9].



yellow
mp 223 °C

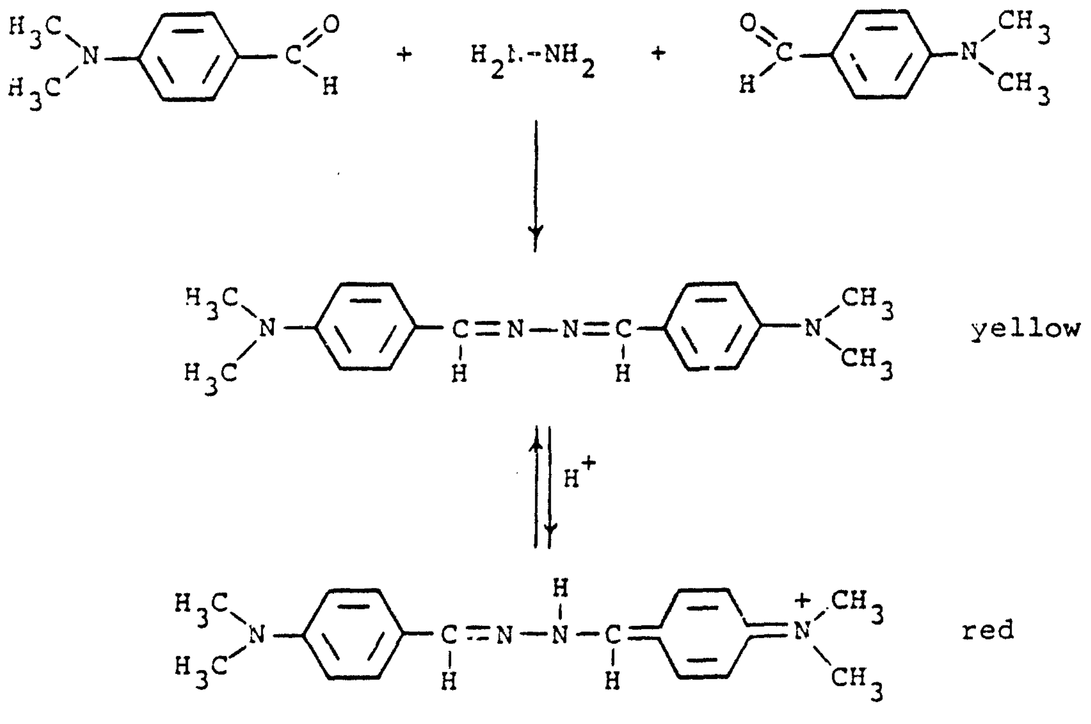
pink
mp 220 °C

cream
mp 220 °C

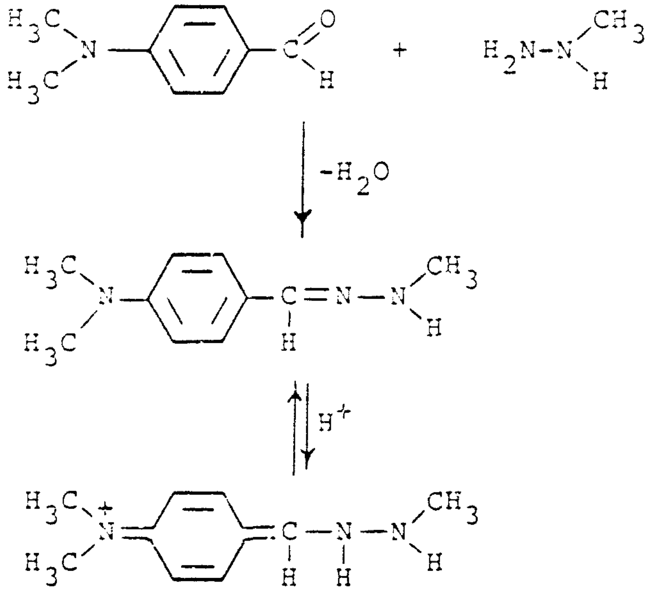
The yellow trans-trans isomer is the predominent, most stable and same "inner complex" structure originally proposed by Feigl.

Salicylaldehyde has also been successfully used in the analysis of hydrazine-monomethylhydrazine-1,1-dimethylhydrazine mixtures by taking advantage of selective precipitation of the salicyladazine and titration of the more basic hydrazone products[10].

2. p-N,N-Dimethylaminobenzaldehyde. Based on his observation of the yellow color associated with the salicyaldazine structure, Feigl predicted useful colorimetric variations for aldazine products from use of colored aromatic aldehydes with dimethylaminobenzaldehyde mentioned in particular[8]. A characteristic color change was observed when an acidic solution of dimethylaminobenzaldehyde and hydrazine are mixed, and has been spectroscopically quantified into a hydrazine analytical method based on a visible absorption at 458 nm[11,12,13]. This absorption conforms well with Beer's Law, has an optimum concentration range of 0.06 to 0.47 ppm and is the basis of an ASTM analytical method for hydrazine[14]. In acid solution, the azine adduct is red and water soluble, while in alkaline or neutral medium, the adduct is yellow and water insoluble. The protonated p-quinone structure is considered to responsible for the 458 nm absorption[11,13].



Interestingly, a colorimetric analysis for methylhydrazine following the same procedure as for hydrazine yielded nearly the same spectral response (i.e. maximum at 460 nm) while, in this case, the condensation must stop at the hydrazone structure[15].



This observation also indicates that the p-quinone structure in the chromophore responsible for the visible light absorption.

The sensivity of this system depends on the conditions of analysis. For liquid sampling sensitivities of 0.1 to 1.0 ppm are typical[11-16]. However, for air sampling, a 10^{-4} ppm sensivity was reported for a solution of dimethylaminobenzaldehyde in 8% H_2SO_4 for 100 liters of air over a 20 minute period[17a].

The Air Force has developed an analytical procedure for hydrazine in air by absorption and concentration of hydrazine vapor in a tube packed with sulfuric acid impregnated firebrick[17b]. The sulfuric acid stabilizes the hydrazine against atmospheric oxidation, and subsequent analysis is performed by reaction with dimethylaminobenzadehyde and spectroscopic measurement of the absorption at 455 nm. A sensitivity of 0.01 to 0.28 ppm for a 15 liter sample of air is reported with interferences reported for aromatic amines, methylhydrazine and phenylhydrazine.

Table 2

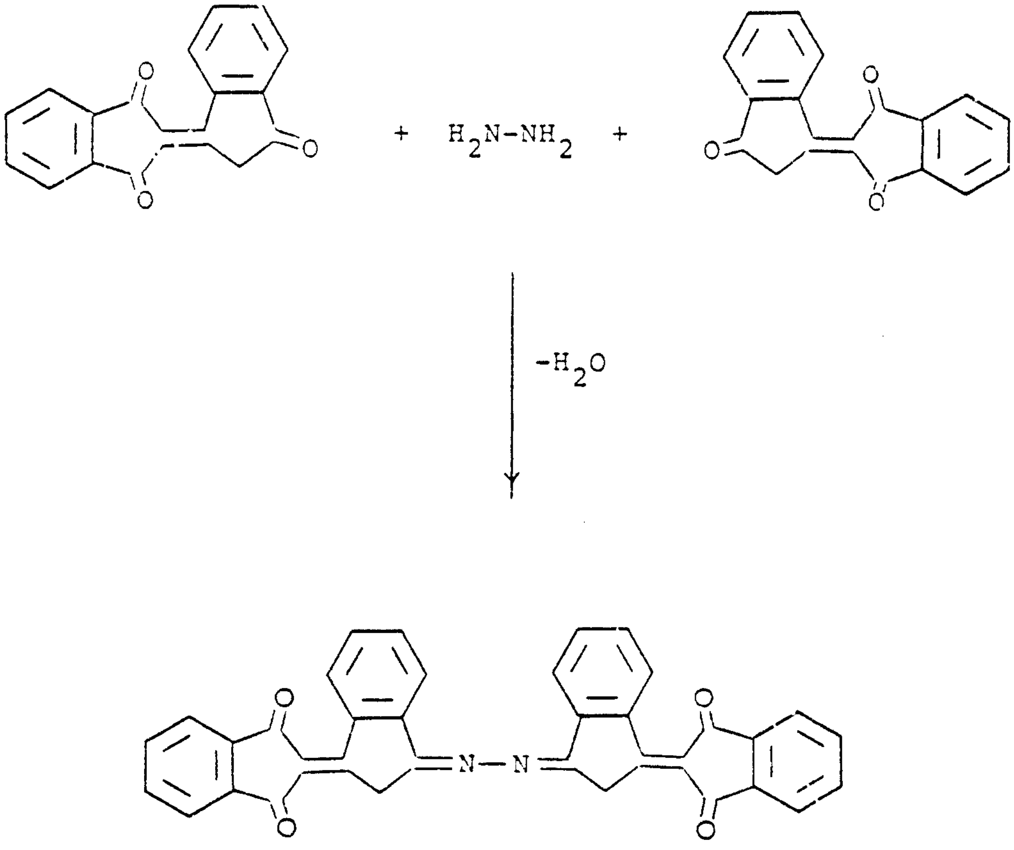
Compounds Tested for Interference with Dimethylaminobenzaldehyde - Hydrazine Analysis

Compound	Interference	Reference
water	none	16
methanol	none	16
ethanol	none	16
methylamine	none	11
dimethylamine	none	11
trimethylamine	none	11
ethanolamine	none	11
choline	none	11
urethane	none	11
aminoguanidine	none	11
hydroxylamine	none	11
phenylhydrazine	none	11
semicarbazide	small	11,12
urea	small	11,12
ammonium ion	none	11,12
1,1-dimethylhydrazine	none	17b

Although the dimethylaminobenzaldehyde condensation can not distinguish between hydrazine and methyl hydrazine, the compounds listed in Table 2 are reported to have a very small or negligable interference.

Discrepancies exist for some of the interference compounds (for example hydroxylamine[11,18], and phenylhydrazine[11,17b] although differing analytical conditions may be involved).

3. Bindone. By adding a higher degree of conjugation to the reactive aldehyde or ketone, a more colorimetrically distinguished azine or hydrazone is obtained from condensation with the hydrazine compound. Anhydrobisindanedione or bindone in glacial acetic acid reacts to form a dark green product which is specifically characteristic of hydrazine[18].

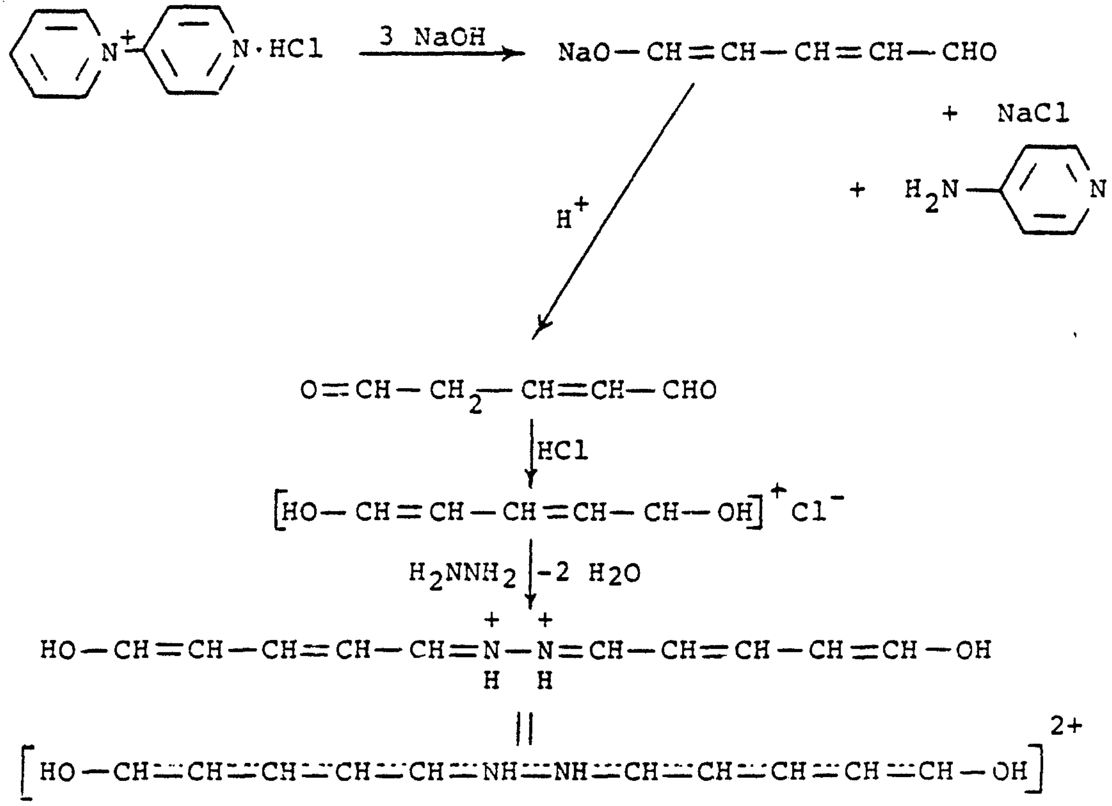


green

A sensitivity of 1:100,000 (10 ppm) is reported. This system is also reported to be free of interference from alkyl and arylhydrazines (methyl-, ethyl-, phenyl-, acetylphenyl-, and dinitrophenylhydrazines). However, primary amines yield a violet or blue colored product with bindone in glacial acetic acid.

Bindone has been reported as the sensitive element in a personal dosimeter for hydrazine, methylhydrazine and 1,1-dimethylhydrazine[19]. The development of a purple color on exposure to these vapors is reported. This is in disagreement with reference 18 although the dosimeter is also composed of a silica gel base and polyvinylalcohol binder which may have altered the chemistry. The sensitivity is 100-200 ppm,with ammonia, amines and cigarette smoke reported as interferences.

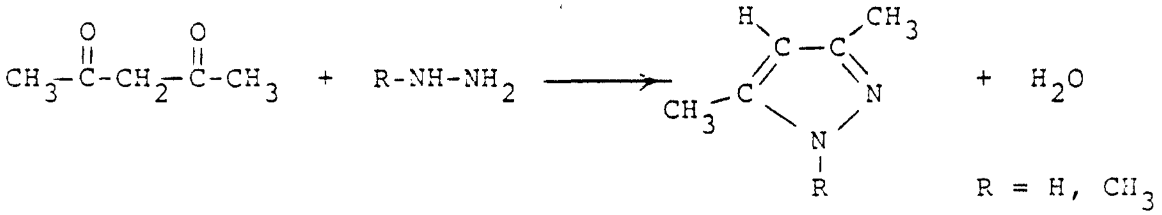
4. Glutaconaldehyde. The reaction of hydrazine with glucaonaldehyde is another way of generating a highly conjugated and colored azine product[20]. Glutaconaldehyde is generated by the alkaline hydrolysis of pyridylpyridium-dichloride followed by acidification. The protonated aldehyde rapidly reacts with hydrazine to produce a red colored product described by the cationic formula below.



red

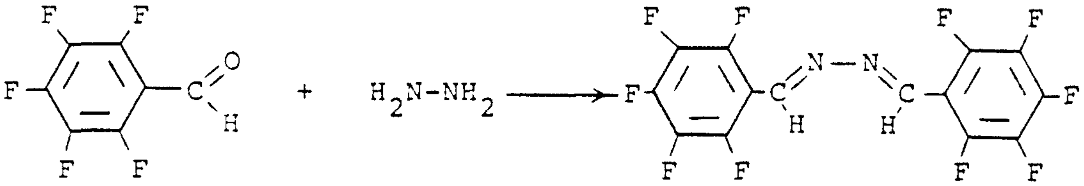
The product has an absorption maximum near 500 nm which conforms to Beer's Law, and the reported sensitivity is 0.005 µg. Substituted hydrazines, hydrazids and hydrazones as well as aromatic primary and secondary amines also react to yield products of different colors ranging from orange to dark red.

5. 2,4-Pentanedione. A facile cyclization reaction between 2,4-pentanedione and hydrazine or methylhydrazine to quantitatively yield a pyrazole product has been used for quantitative analysis by gas chromatography[21].

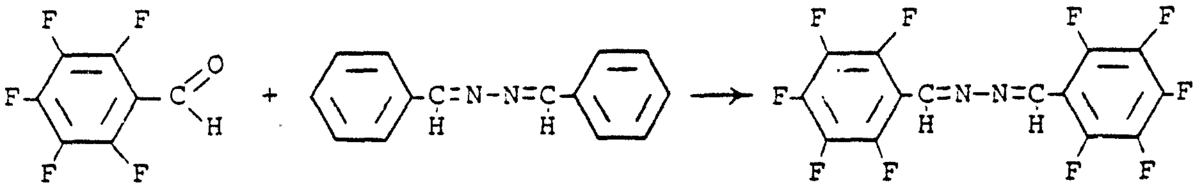


The pyrazole products are formed under mild conditions (neutral aqueous solution, room temperature) and chromatograph well on a variety of columns. A sensitivity range of 0.5 to 50 ppm was reported with no interferance from 1,1-dimethylhydrazine, urea or D,L-alanine.

6. Pentafluorobenzaldehyde. Reactivity of an aromatic aldehyde or ketone toward nucleophilic addition may be enhanced by attachment of electron withdrawing substituents. Pentafluorobenzaldehyde has been used to trap hydrazine in a reactive cigarette smoke mixture and the fluorine substitution makes possible detection of nanogram quantities of the azine product by gas chromatrography with electron capture detection[22].



Of additional interest is an exchange reaction between benzaldazine and pentafluorobenzaldehyde.

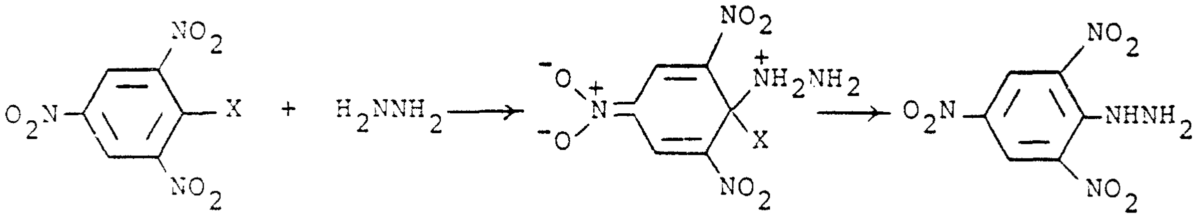


This is a good example of the trade-off between specificity and sensitivity.

7. <u>Phthaldehyde</u>. The reactivity of a benzaldehyde functional group toward nucleophilic addition is enhanced by the presence of a second aldehyde group. The high reactivity and resultant fluorescence of ortho, meta and para phthaldehyde with hydrazine form the basis of a chemical spot test with nanogram sensitivity[23]. With the ortho and para phthaldehydes the fluorescence is blue while the meta derivative is brown in fluorescence and less sensitive. This test is negative for 1,1-dimethylhydrazine and appears to offer discrimination of other hydrazines. Unfortunately, the products are not characterized as to structure.

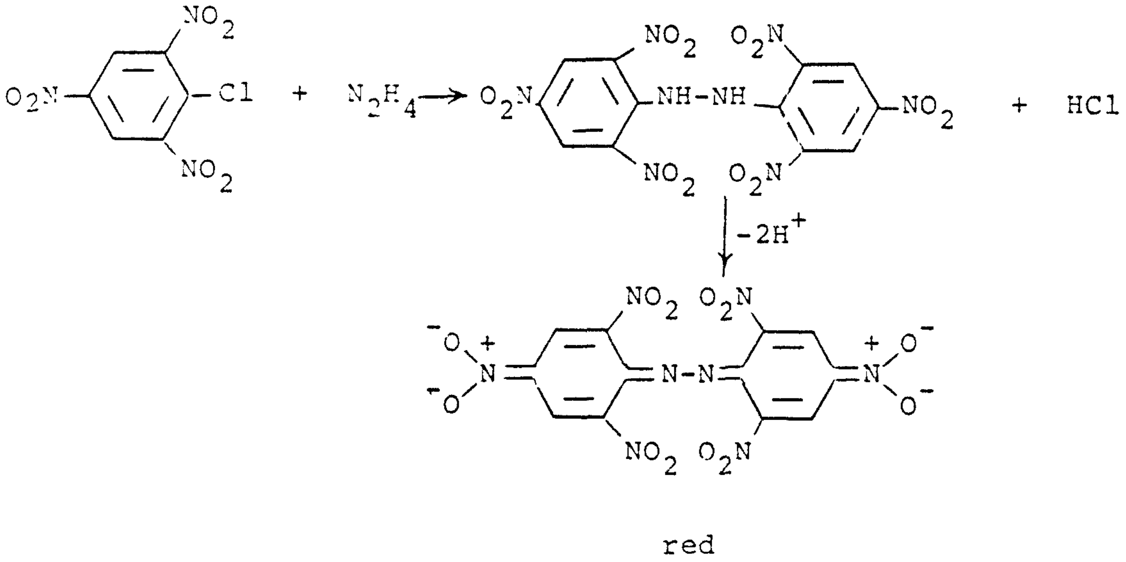
3. NUCLEOPHILIC AROMATIC DISPLACEMENTS.

Like the aldehyde and ketone condensations of the previous section, the nucleophilic aromatic displacement reactions of this section depend on the aminelike nucleophilicity of the hydrazine compound. The aromatic substrate is functionalized a displaceable group, x, and strong electron groups, usually nitro groups, which activate the compound. The nitro groups also stabilize the intermediate, called a Meisenheimer salt, which is frequently isolated. The two step mechanism is depicted as follows.



While this reaction is not exclusive toward amines, it does yield products with a great variety of color. The color is dependent on the structures of the nitro aromatic substrate and nucleophilic agent. The reactions conditions are neutral or basic media.

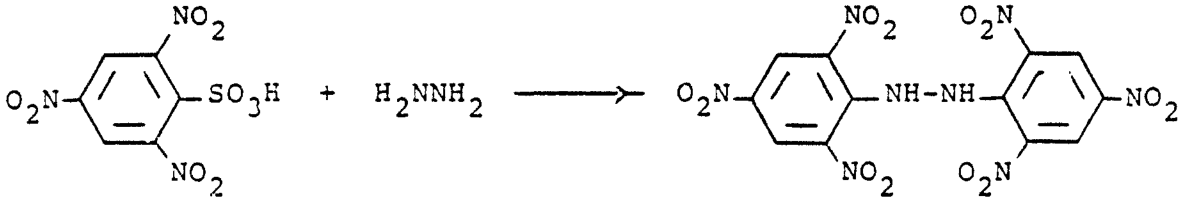
1. Picryl Chloride. The first nitro aromatic compound to be used for hydrazine detection was picryl chloride[24,25].



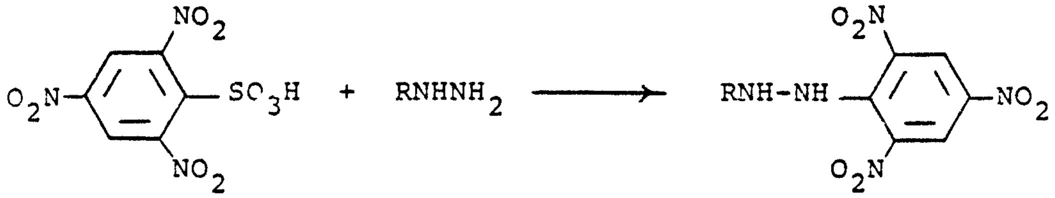
red

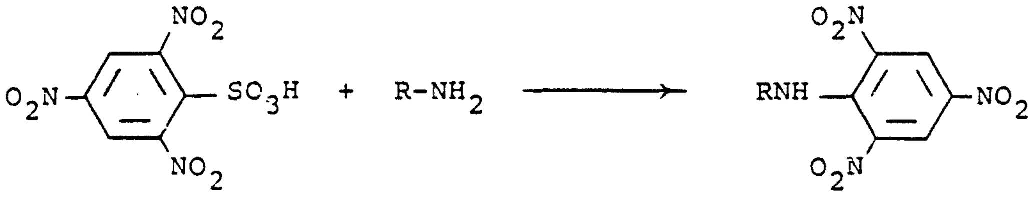
The bistrinitrophenylazine develops a red color in the presence of a borate or acetate buffer. This absorption follows Beer's Law to a lower limit concentration of 0.2 ppm and is nearly pH insensitive between values of 3.5 and 10. Small interferences were noted from chloride ion and hydroxyl amine, and a major interference was noted from the azide ion.

2. Trinitrobenzene Sulphonic Acid. Trinitrobenzene sulphonic acid was found to be superior to picrylchloride, which is unstable in aqueous solution toward precipitation. Trinitrobenzene Sulphonic acid solution selectively reacts in weakly alkaline solutions with hydrazine, monosubstituted hydrazines and primary amines[26].



violet





The hydrazine adduct is violet, while the monosubstituted hydrazine and primary amine adducts are yellow, orange or pink. Disubstituted hydrazines do not react. The hydrazine and methylhydrazine detection limits were 0.02 and 0.2 μg respectively. A total of 55 compounds were tested.

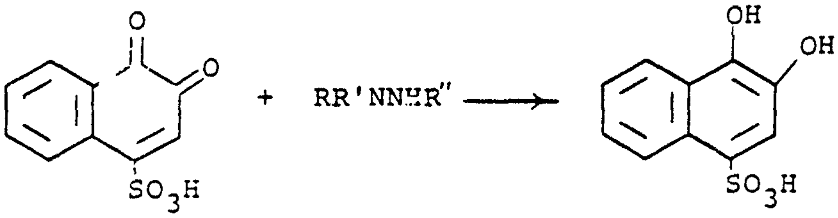
4. <u>2,4-Dinitrofluorobenzene</u>. 2,4-Dinitrofluorobenzene was selected from a collection of 49 nitroaromatic compounds as a colorimetric indicator of hydrazine that can differentiate it in the presence of hydroxyl amine[27]. In acidic and basic medic the response to hydrazine is yellow and green, while that for hydroxyl amine is orange and red respectively. The detection limits were 10 μg for hydrazine and 6 μg for hydroxyl amine. Other substituted hydrazines could not be distinguished from hydrazine.

5. <u>General Nitro Aromatic Compounds</u>. For the purpose of developing a colorimetric array for qualititative analysis of hydrazines and amines, Malone investigated the colorimetric response of 20 nitro aromatic compounds to hydrazine, methyl hydrazine, 1,1-dimethylhydrazine and 9 mono and multifunctional amines with varying degrees of substitution[28]. The compounds were contacted in pure form and 11 different colorimetric responses were tabulated. The results suggested that both qualitative and semiquantitative analysis of hydrazines and amines in air drawn through glass tubes containing these nitro aromatic compounds could be performed by analysis of the array of colorimetric responses.

4. ORGANIC COMPOUND AND METAL ION REDUCTIONS.

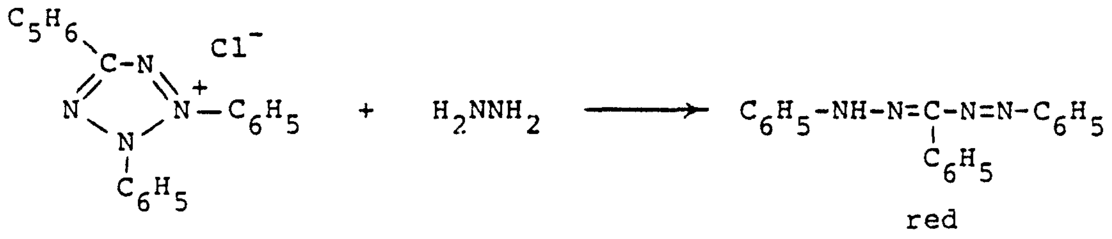
In synthetic chemistry, hydrazine is widely used as a reducing agent for nitro, nitroso, carbonyl, nitrile, alkene and alkyne compounds. These reactions usually require very specific conditions and catalysts. The reduction of metal ions to lower valance states is usually less condition specific and does not require catalysts. Hydrazine is oxidized by way of a variety of mechanisms. Reference 3 should be consulted for details. Organic compounds that are good candidates for spot tests are those which undergo a facile reduction with a coincident color change. Quinones and triones are good examples. Numerous metal ions have been reduced to lower valence states or to neutral metals[29]. The pH of the medium is an important consideration since neutral hydrazine is oxidized more easily than the hydrazinium ion.

1. 1,2 Naphthoqunone-4-sulfonic acid. The reduction of 1,2-naphthoquinone-4-sulfonic acid to the fluorescent dihydroxynaphthalene product has been reported to be a sensitive assay for hydrazines in mixtures of biological origin such as blood plasma and urine[30].



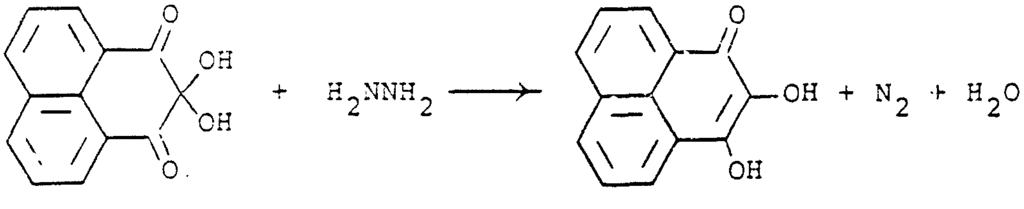
The fluorescence emission maximum is at 440 nm (excitation at 360 nm), and the pH dependent maximum is at 6.5. The reduction is specific to hydrazine, monoalkylhydrazines, and both N_1N_2- and N_1N_1-dialkylhydrazines, but reduction does not occur with acyl and acylalkylhydrazines. Sensitivities as high as 0.1 µg/ml are reported.

2. Triphenyltetrazolium chloride. The reductive ring opening of triphenyltetrazolium chloride by hydrazine in alkaline media has been reported as a colorimetric analysis for hydrazine[31].



The triphenylformazane product is red, and the absorption follows Beer's Law. The detection limit for hydrazine is 0.5 mg.

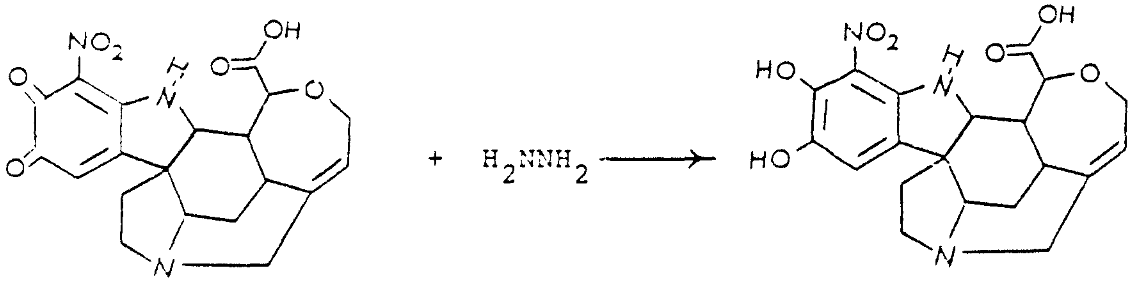
3. Peri-naphthindan-2,3,4-trione hydrate. Peri-naphthindan-2,3,4-trione hydrate is reduced by hydrazine compounds to the dihydroxy-peri-naphthindenone in acid media[32].



red

The trione hydrate is colorless, and dihydroxy product is red with a visible absorption maximum at 460 nm. The reaction is positive for methyl and phenyl hydrazinium salts and free of interference from amino compounds, amides, acids, hydroxy compounds, carbonyl compounds, carbohydrates and thiols. However small amounts of benzidine, semicarbzide, pyrogallo and ascorbic acid interfere. The detection limits are 1 µg as a spot test and 0.1 to 0.6 µg by spectroscopic analysis.

4. Cacotheline. Cacotheline, a natural product derivative, is a dione activated by a nitro group and is reported as a sensitive spot test reagent for hydrazine in alkaline media[33].



blue

Reduction causes development of a deep blue color. The hydrazine detection limit is 6 µg/3 ml.

5. Silver Nitrate. As a spot test, reduction of silver ion impregnated in filter paper has a sensivity limit of 0.05 μg to hydrazine in alkaline solution[34]. The test requires removal of brown silver oxide by washing with ammonia water to observe the black silver precipitate. Hydroxyl amine and other reducing substances interfere with this test.

A sensor based on the reduction of silver and gold salts deposited out very thin metal films has been patented[35]. The reduction of the noble metal salt by the reducing agent vapor causes a conductivity increase in the thin metal film. Hydrazine and 1,1-dimethylhydrazine sensitivities of 10 to 100 ppm are reported.

6. Molybdenum Blue. Phosphomolybdic acid or molybdic acid in combination with other acids can be converted to molybdenum blue by a variety of reducing agents[36]. The development of blue color is associated with a partial reduction in molybdenum valence between 6 and 5, and the composition and structure of the blue species is not well-defined[37]. Combinations of molybdic acid and other acids coated on granular silica gel have been patented as having 1 to 10 ppm detection level sensitivities to hydrazine, methylhydrazine and 1,1-dimethylhydrazine vapors[38]. The MDA Scientific, Inc. Autospot hydrazine analysis is based on optical reflectance monitoring of paper tape impregnated with phosphomolybdic acid for blue color development caused by exposure to hydrazine vapors. This device was evaluated by the Air Force and found to have sub ppm level sensitivities to hydrazine and its methyl derivatives while being free of positive interference from nitrogen dioxide, ammonia, sulfur dioxide and phosgene although ammonia and aniline deactiviated the tape[39].

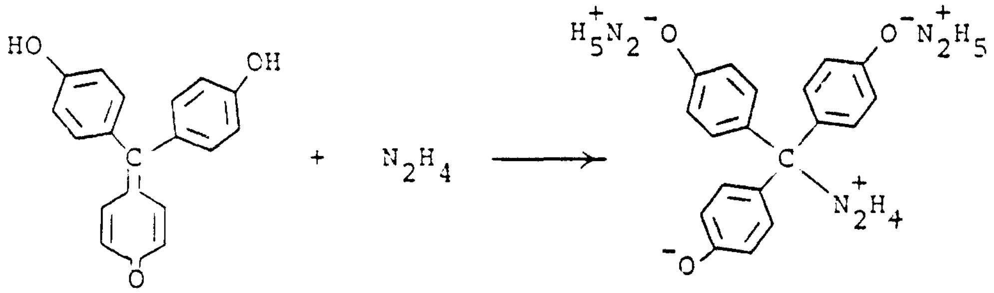
7. Ferrozine. Iron (III) in the presence of the disodium salt of 3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine, "Ferrozine", in aqueous acid is reduced by hydroxylamine, hydrazine, methylhydrazine and 1,1-dimethylhydrazine with coincident development of a visible absorption at 562 nm[40]. This reaction with hydroxylamine is much more rapid than with hydrazine, and each may be individually analyzed by time dependent spectroscopic measurements. The sensitivity ranges from 1 to 10 μg/25 ml, and interference is observed from substances capable of reducing iron (III) (iodide, ascorbic acid, cysteine, semicarbazide, etc.).

5. ORGANIC DYE OPTICAL AND ELECTRICAL RESPONSES.

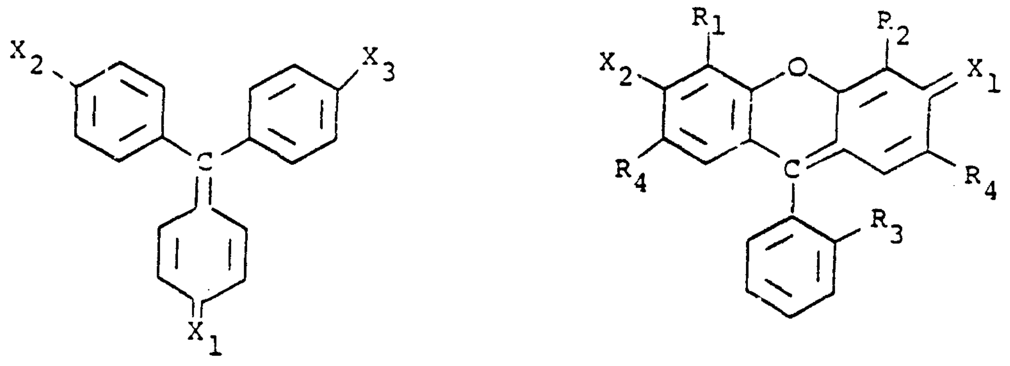
The large conjugated structure of an organic dye is associated with physical and chemical properties that are particularly useful for detection purposes. Physically, the structure is responsible for lower oxidation and reduction potentials and for lower energy electronic transitions. These molecular features are observed macroscopically as electrically semiconducting and visually optical properties. Chemically, dyes are very active. Molecular interactions ranging from molecular association to covalent bond formation are observed and usually classified as electron donor and electron acceptor interactions. The degree of interaction between a dye and a vapor and of consequent physical property modulation is dependent on the chemical nature and concentration of each component. Often these interactions are reversible. For vapor detections, dyes are attractive as chemical interfaces for microsensors since small optical and electrical property changes may be measured, and a variety of reversible responses to different vapors is possible.

1. Triphenylmethane and Xanthene Dyes. Triphenylmethane and xanthene dyes may be represented by the following general structures with specific examples having the substitutions as indicated (see Figure 1)[41].

In the 1960's, interactions between triphenylmethane and xanthene dyes with hydrazine were extensively described in the Russian Literature[42]. The interactions were primarily characterized by the electronic and infrared spectroscopies and electrical and photoelectrical measurements. Two types of molecular interactions were described; one involving nucleophilic addition to the central carbon atom and the other as a deprotonation of a peripheral phenolic or carboxylic group. Using aurin as the example, the following reaction scheme has been proposed.



The conjugation between phenolic groups is disrupted. In the electronic spectrum of the aurin dye film exposed to 1 to 2 mm hydrazine, the visible absorption at 494 nm disappears. In the infrared spectrum, intense bands characteristic of a conjugated



Triphenylmethane Dye

Xanthene Dye

Fucnsin

$X_1, X_2, X_3 = NH_2$

Crystal Violet

$X_1, X_2, X_3 = N(CH_3)_2$

Malachite Green

$X_1, X_2 = N(CH_3)_2$

$X_3 = H$

Aurin (Rosolic Acid)

$X_1 = O$

$X_2, X_3 = OH$

Fluorescein

$X_1 = O$; $X_2 = OH$; $R_3 = CO_2H$

$R_1, R_2, R_4 = H$

Gallein

$X_1 = O$; $X_2 = OH$; $R_3 = CO_2H$

$R_1, R_2 = OH$; $R_4 = H$

Rhodamine 6G

$X_1, X_2 = NH(C_2H_5)$; $R_3 = CO_2C_2H_5$

$R_1, R_2 = H$; $R_4 = CH_3$

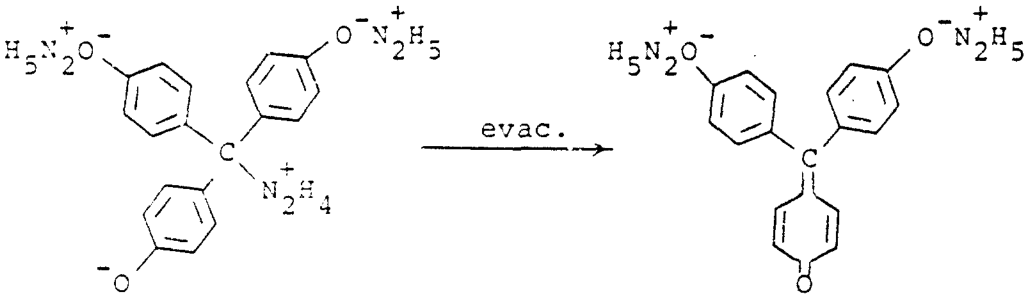
Eosin

$X_1 = O$; $X_2 = OH$; $R_3 = CO_2H$

$R_1, R_2, R_4 = Br$

Figure 1. Structures of Triphenylmethane and Xanthene Dyes.

triphenylmethane system (1594, 1360 and 1165 cm^{-1}) are displaced by non-conjugated phenyl absorptions (1610, 1510 and 1267 cm^{-1}), and N-H bonds are observed. The colorless quasileuco adduct is reported to exhibit no appreciable conductivity although, at hydrazine pressures greater than 0.8 mm, an ionic conductivity attributed to the ionic dye solvated by hydrazine was observed. When the dye film is subjected to a high vacuum or gently warmed, the color and spectra are partially restored but differ from the original since the phenolic groups have formed a hydrazinium adduct.



Stronger heating (>60°C) will restore the aurin visible spectrum indicating the binding of hydrazine to the hydroxyl group is stronger than to the central carbon.

No application for hydrazine vapor detection was mentioned in this triphenylmethane-xanthene dye literature.

2. Phthalocyanine Dyes. Phthalocyanine dye compounds are characterized by a conjugated 16 membered 18 π electron macrocyclic structure with a cavity which may be occupied by two protons or a variety of metal ions. There is a strong coupling between the π system of the phthalocyanine ligand and the metal ion which facilitates oxidation and reduction of the entire complex. Further, the axial orbitals of the transition metal ions are capable of chemisorbing labile ligands (i.e. hydrazine) and facilitating reaction catalysis. (See Figure 2)

Hydrazine has played a very important role in the study of phthalocyanine redox chemistry; some aspects of which are particularly pertinent for the detection of hydrazine vapors. The key points will be chronologically summarized here.

In 1964, it was discovered that ferrous phthalocyanine could be reduced with a corresponding color change from blue to red by reaction with 2-propoxide in basic alcohol[43].

$$FePc + (CH_3)_2CHO^- \longrightarrow [HFePc]^- + (CH_3)_2CO$$

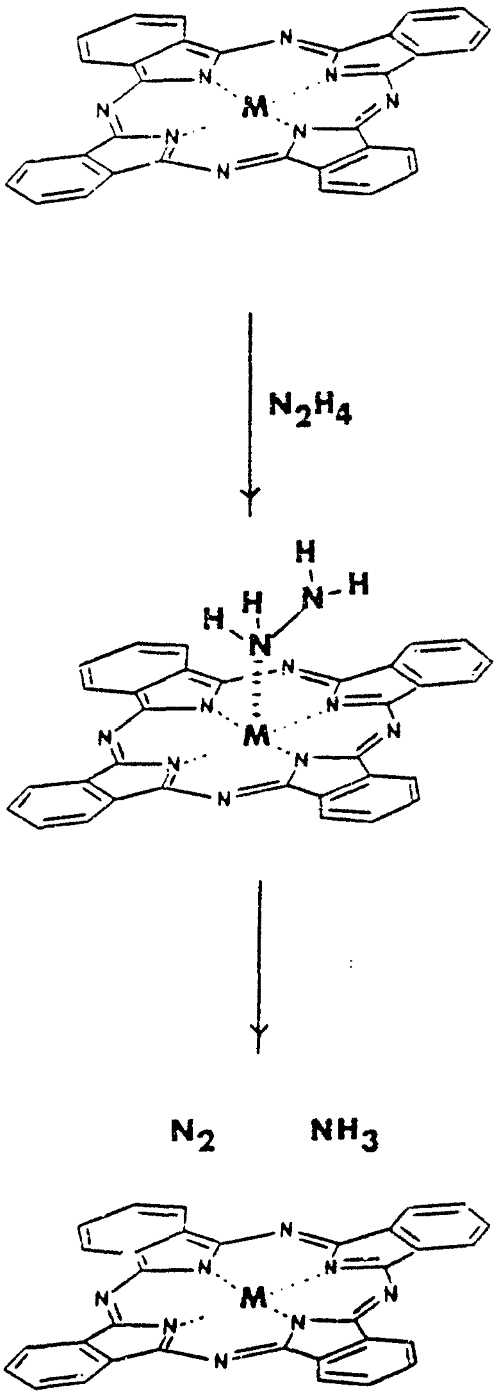


Figure 2. Phthalocyanine catalyzed decomposition of hydrazine.

Admission of oxygen restored the original ferrous phthalocyanine. Other hydride reducing agents (sodium brohydride and ethyl magnesium bromide) are also effective on Fe(II) as well as Mn, Co, Ni and Cu phthalocyanines. Since the visible spectrum was markedly changed, it was suggested that the reduction involved addition of an electron to the phthalocyanine ligand.

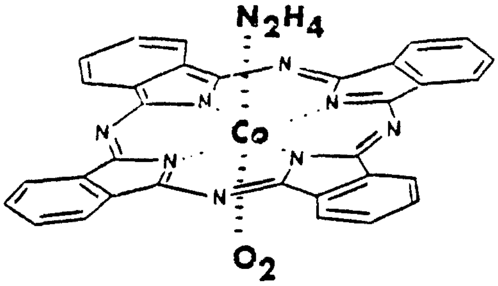
Later that year, another study on the reduction of cobalt (II) tetrasulfophthalocyanine, Co(II)tsp, by hydrazine in near neutral medium appeared[44]. The color change was from deep blue to yellow-green. Susceptibility measurements indicated the reduced cobalt phthalocyanine to be diamagnetic and a Co(I) phthalocyanine complex was proposed.

In 1968, the reaction of cobalt phthalocyanine with hydrazine was more closely examined using ESR and PMR to characterize the valence state of cobalt[45]. The reaction of CoPc with hydrazine in pyridine/dimethylacetamide caused a color change from blue to yellow. The yellow solution displayed no ESR signal indicating the Co(II)Pc had been reduced to Co(I)Pc. When methyl iodide was added, a color change from yellow to blue was observed but no new ESR signal was detected. The PMR spectrum had a single resonance at $\delta=-6.1$ ppm indicating a methyl group is axially bound to a Co(III)Pc. Irradiation with UV light restores the Co(II)Pc. The reaction sequence was summarized as follows.

$$\mathrm{Co^{II}Pc} \xrightarrow{\mathrm{N_2H_4}} \mathrm{Co^{I}Pc} \xrightarrow{\mathrm{CH_3I}} \mathrm{Co^{III}CH_3Pc} \xrightarrow{h\nu} \mathrm{Co^{II}Pc}$$

Each cobalt phthalocyanine compound has a distinctively different electronic spectrum.

In 1973, the mechanism by which Co(II)Pc catalyses the oxidation of hydrazine in the presence of oxygen was studied[46]. The Co(II) derivative was found to be 2 to 3 orders of magnitude more active than the Fe (III), Mn (III), Cu (II) or Ni (II) derivatives. A careful study was made of absorption spectral changes when hydrazine and oxygen were added to alkaline solutions of cobalt tetrasulfophthalocyanine. Contrary to previous studies, addition of hydrazine was reported to result in formation of a stable 1:1 Co(II)tsp: hydrazine complex, which is green in color. Oxygen has been reported to form a 1:2 Co(II)tsp:O_2 complex[47]. The data appears to indicate that hydrazine and oxygen may reversibly displace one another depending on their relative concentrations. The oxidation of hydrazine required a pH greater than 12 and the addition of oxygen. The proposed mechanism invoked formation of a trans octahedral ternary CoPc:N_2H_4:O_2 complex where an undefined electron transfer between hydrazine and oxygen is mediated by the cobalt ion and π electron system of the phthalocyanine ring.



Later work, involving ESR spectral changes when hydrazine was added to an aqueous/dimethylformanide solution of Co(II)tsp showed characteristic hyperfine structure of the blue Co(II)tsp: 2 O_2 and green Co(II)tsp: N_2H_4 complexes and demonstrated their reversible concentration dependent displacements at pH < 11.5[48] At pH > 11.5 irreversible oxidation of hydrazine and formation of Co(I)tsp occurs by electron transfer to Co(II). The pH dependence is attributed to the more facile oxidation of unprotonated N_2H_4 as compared with $N_2H_5^+$ ligand. More recently, the interaction and oxidation of hydrazine vapor with solid-state bivalent H_2, Mn, Fe, Co, Ni, Cu, Zn, and Pd phthalocyanine films has been studied[49,50]. In the absence of oxygen these phthalocyanine compounds catalyze decomposition of hydrazine to nitrogen and hydrogen or ammonia with conversions ranging from 2% to 100% at 550°K as determined by gas chromatographic analysis of the products.

MPC	H_2	Ni	Cu	Mn	Co	Fe	Zn
% conversion	2	4	12	77	98	100	100

The experiment was also performed with hydrazine hydrate, $N_2H_4 \cdot H_2O$, with similar results.

MPC	H_2	Pd	Ni	Cu	Mn	Co	Fe	Zn
% conversion	2	2	5	5	13	20	100	100

The metal ions that have vacant (Fe II, Mn II) or half filled (Co II) dz^2 orbitals are capable of axial coordination with an electron lone pair of hydrazine for complex formation and subsequent catalysis. For the exceptional case of the Zn ion a shift from a square planar to a square pyrimidal configuration was proposed. (This would appear to involve a 4s orbital.)

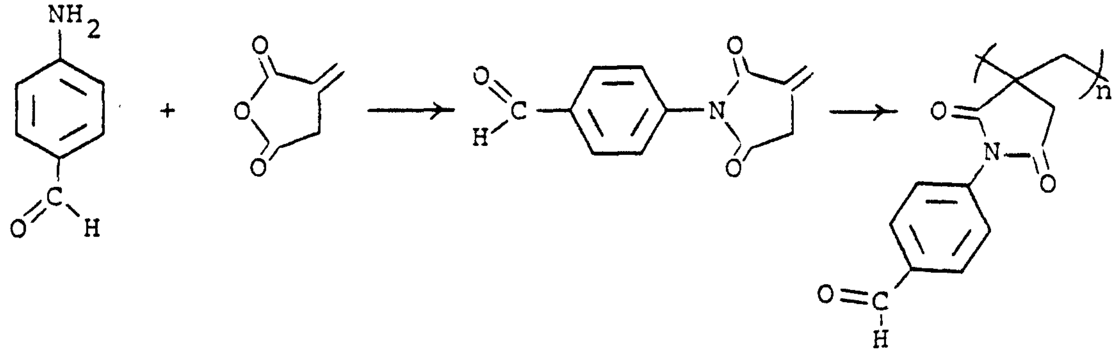
Initial complex formation of hydrazine vapor with iron (II) phthalocyanine was studied by infrared spectroscopy[50]. An initial physisorption of the hydrazine on the crystal surface followed by a chemisorption was detected as an initial 3265 cm^{-1} N-H absorption followed by the appearance of N-H bands at 3140 and 3365 cm^{-1}. The band at 3265 cm^{-1} was assigned to physisorbed hydrazine while that at 3365 cm^{-1} was assigned to chemisorbed hydrazine. The interpretation for the N-H band shift was that the N-H bond is weakened by an electron withdrawal effect which is induced by coordination bonding of nitrogen with the metal ion. The complex is stable at room temperature under 10^{-2} torr but liberates hydrazine to regenerate the infrared spectrum of the initial iron phthalocyanine film when subjected to 10^{-4} torr or heated to 450°K. Regarding the effect of crystal structure, the α crystalline form was found to admit hydrazine for complex formation more rapidly than the β form.

6. DETECTION SCHEMES.

In this section specific experimental approaches to the design and synthesis of hydrazine sensitive thin film coatings are outlined. The concepts are closely related to those presented in previous sections and range from simple polymeric binder formulations of well-known analytical systems to new and somewhat speculative systems. It should be noted that many of the analytical reactions presented occur in uniphase liquid solutions while our application as a solid-state vapor sensor is a heterogeneous gas-solid system. The presumption is that similar chemistry will occur when suitable solid-state polymeric binders are employed to mimic the solution reaction medium. The systems targeted for the microsensor subtrates were described in the introduction (i.e. surface acoustic wave device, optical wave guide and chemiresistor).

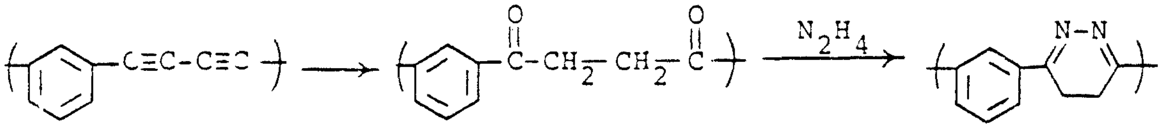
1. Aldehyde Condensation in Poly(acrylic acid) Binder. This approach involves use of poly(acrylic acid) as a thin film dispersing binder for salicyladehyde, p-dimethylaminobenzaldehyde or phthaldehyde, as a carbonyl protonating agent to promote the condensation reaction and as a strong physical absorber and concentrater of hydrazine vapors by way of hydrogen bonding and high polarity. The intense yellow and orange azine adducts with the respective salicylaldehyde and p-dimethylaminobenzaldehyde have microgram colorimetric sensitivities[8,14], while the fluorescence from the hydrazine-phthaldehyde adduct is reported to have nanogram sensitivity[23] (see section 2). Sensitivity amplification by use with the optical wave guide has promising application as a personal dosimeter.

2. Poly(imidbenzaldehyde). A new monomer and polymer would be synthesized by condensation of p-aminobenzaldehyde with itaconic anhydride and vinyl polymerization.



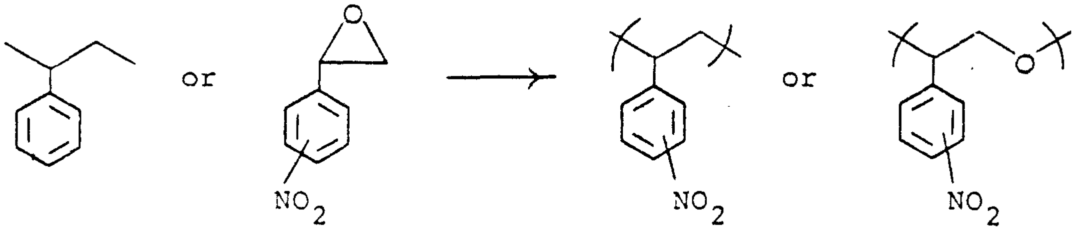
The electron withdrawing influence of the imid group should activate the aldehyde for condensation with hydrazine, and the conjugation of the imid group with the azine or hydrazone adduct should promote an intensely colored product. Direct attachment of the imidbenzaldehyde group to the polymer matrix provides a more stable polymer film and allows for a higher concentration of the reactive functional group when compared with occlusion in a binder. If acid catalysis is necessary to activate the aldehyde, copolymerization with acrylic acid (or its methyl ester) could be performed.

3. Conjugated Poly (α,δ-diketone). This approach involves hydration of poly(m-diethynylbenzene) to the α,δ-diketone, which, on reaction with hydrazine, would form a stable six-membered 4,5-dihydro-1,2-diazine ring and reconjugate the main chain benzene rings.



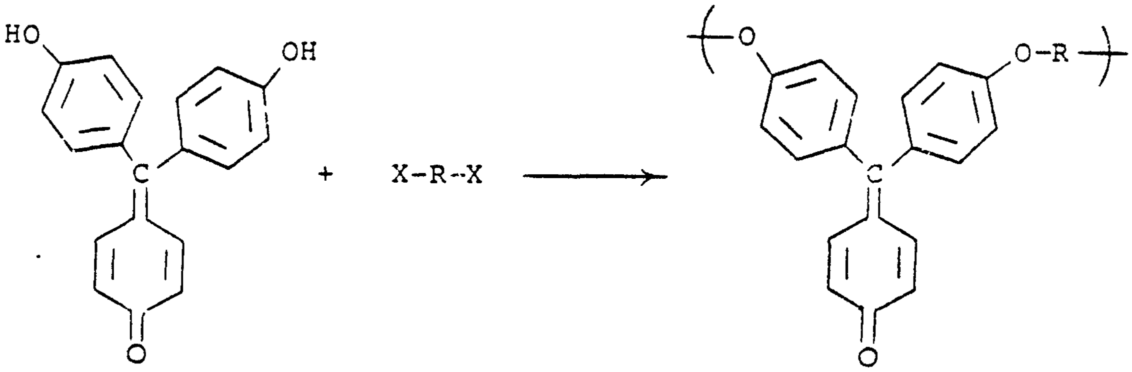
Physically, this transformation should have a color developing and conductivity enhancing effect which may be detectable with the optical wave guide, chemiresistor or surface acoustic wave device substrates.

4. Nitroaromatic Polymers. Variation in the degree of nitro and alkyl substituents in nitroaromatic compounds result in numerous different colorimetric responses on exposure to amines and hydrazines[28]. A wide variety of thin film forming amorphous polymers may be prepared by simple nitration of the aromatic polymers (e.g. polystyrene) or polymerizing nitroaromatic monomers (e.g. nitrostyrene oxide).



An array of nitroaromatic coatings with different responses to hydrazines and amines could easily be generated by variation in the degree of nitration. Further, poly(nitrophenylacetylenes) have been prepared as organic semiconductors which suggests an electrical as well as colorimetric response could be used for detection.

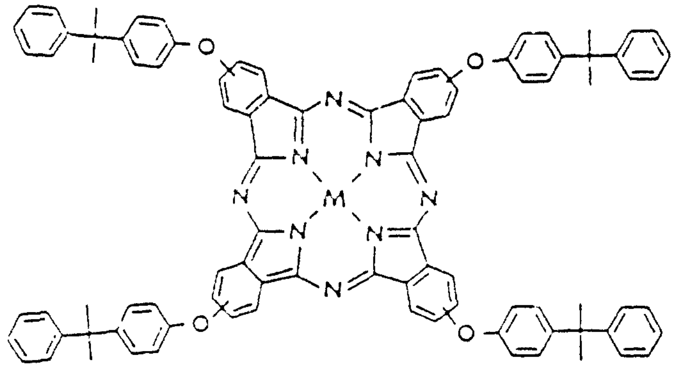
5. Rosolic Acid Polymers. Formally, rosolic acid (aurin dye) is an aromatic diol with a strong Lewis acid carbon center. Aromatic diols are readily converted into polyesters, polyethers and polyformals.



X = halogen
(a) R = $-CO(CH_2)_nO-$
(b) R = $-(CH_2)_n-$
(c) R = $-CH_2-$

The Lewis acid carbon center is preserved, and it should interact reversibly with hydrazine vapor in a similar manner as is reported for the monomer[42]. A polymer coating prepared from this monomer should display responses to hydrazine that are detectable by the surface acoustic wave device, optical wave guide and chemiresistor substrates.

6. Phthalocyanine Dyes. Work involving the electrical response of phthalocyanine films to hydrazine vapor is currently in progress. The approach is to deposit the phthalocyanine chromaphores as mixed Langmuir-Bladgett monolayers and multilayers. An important feature of this technique is a uniform and reproducible film deposition. The required phthalocyanine solubility is achieved by tetracumylphenoxy peripheral substitution.



M = H_2, Mg, Co, Ni, Cu,
Zn, Pd, Pt, Bi, Pb

The substituent size and positional isomerism (2 or 3 position of each benzo ring) contribute toward an open and vapor accessible matrix. At present electrical response measurements to hydrazine vapors are being made. It would be of interest to supplement the work with some spectroscopic measurements to determine for the various metal substituted phthalocyanines whether complex formation and/or catalytic hydrazine decomposition is occurring as is reported in the literature for sublimed films[49,50].

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