

- I. A SEARCH FOR ORGANIC COMPOUNDS AS COLORIMETRIC QUANTITATIVE REAGENTS FOR INORGANIC IONS.
- II. A STUDY OF THE REACTION BETWEEN 2 ACETAMINO 6 AMINO BENZO THIAZOLE AND CHLOROIRIDIC ACID.

by

JESSE ROLAND NOELL

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Head of Department

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PART I

A SEARCH FOR ORGANIC COMPOUNDS AS COLORIMETRIC
QUANTITATIVE REAGENTS FOR INORGANIC IONS

INTRODUCTION

In the manufacture of almost any substance, material, or article in industrial, pharmaceutical, medical, biological, and research chemistry, in times of peace as well as times of war, analytical chemical methods, because they give information which is unobtainable by other means, have become of very great importance.

In all applied chemistry, the demand for accuracy in analytical methods varies with the material, application, or condition in each case. Accuracy greater than the conditions of materials warrant, especially if it is at the expense of time, labor, or equipment, is never in demand, since it serves no useful purpose. The great demand in all fields of applied chemistry is for analytical methods of sufficient accuracy which require but little time for completion. In recent years another requisite has been added to that of sufficient accuracy and rapidity, namely that of sensitivity, so that small amounts of substances can be analyzed or determined, if necessary.

Ordinary gravimetric analyses could and can comply with only one of the above qualifications, namely, accuracy.

While here and there a volumetric method will fulfill all the above requirements, especially that of rapidity and occasionally that of sensitivity at the cost of tediousness, the greatest progress in fulfilling these requirements has been that of photometric analysis - colorimetry and nephelometry.

It was this purpose that led the investigator, in cooperation with Randolph-Macon College, Washington and Lee, Virginia Military Institute, Mary Baldwin, Hampden Sidney, William and Mary, and University of Virginia, to search for new organic reagents that may be used for colorimetric analysis in inorganic ions.

Other important information that may be derived from such an investigation may be; new organic indicators, oxidation and reduction reagents, and information which may be of use in predicting color reactions with certain types of organic reagents.

THEORETICAL

There are ninety definitely known chemical elements. A few of these form colored ions in solution. An examination of the periodic table will show that the elements which have the property of forming colored ions occur, for the most part, closely associated with respect to their atomic numbers. Namely, beginning with titanium, atomic number 22, and proceeding to copper, atomic number 29, we find these elements yielding colored ions. To this list we must add a few others, cerium, number 58, gold, number 79, etc. Although the colors of these ions could be made the basis of quantitative colorimetric methods, they are not so used for the reason they would yield only approximate values and, fortunately, in every instance we have other color reactions more highly sensitive and more suitable for colorimetric work. Some of these color reactions are inorganic; others are organic.

Unfortunately, we have little information which will enable us to predict color reactions with organic reagents. It is true that certain types of compounds or certain groups under certain conditions have been found frequently to yield color reactions, especially with metal ions.^{1, 2} However, this information is very limited and it narrows down to the fact that in searching for new color reactions it is necessary to actually try out the prospective reagents with the various metallic and non-metallic ions.

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1. Feigle, F., *Ind. Eng. Chem., Anal. Ed.*, 8, 401-410 (1936)
 2. Sarver, L. A., *J. Chem. Educ.*, 13, 511-514 (1936)

EXPERIMENTAL PROCEDURE

In carrying on such an investigation it is most important that a systematic procedure be followed if the information obtained is to be of scientific value. The following proposed "Micro-technic for the Search of New Organic Color Reactions"¹ was followed.

Solutions of known concentrations of the ions of practically all the elements (except the gases) are arranged according to their atomic numbers in the periodic table. A concentration of one mg. per ml. is convenient for a standard solution. These should be prepared from a salt of a high degree of purity. In most cases aqueous solutions are satisfactory, but in a few instances acid solutions are required in order to prevent hydrolysis. Each reagent bottle carries a calibrated dropper tipped with a rubber cap. A dropper which delivers about 20 drops per ml. is convenient, since each drop will contain about 0.05 mg. of the constituent to be investigated. Single drops of each solution are placed in 0.5 ml. glass cells such as those used in the Brown² drop method for the determination of pH colorimetrically. To each of these glass cells is added a drop of one of the ion solutions. A drop of the organic reagent solution is then placed in each cell and observation made as to the presence or absence of color formation. In case one or more color reactions are obtained, then it is necessary to observe the various characteristics such

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1. Yoe, J. H., J. Chem. Educ. 14, 170-173 (April, 1937)
 2. Brown, J. H., J. Lab. Clin. Med., 9, 239 (1924)

as color intensity, the shade or tint of color, rate of fading, or increase in sensitivity, if any. If, perchance, only a few ions yield color reactions and the color is rapidly formed and is reasonably stable, then the reaction offers a possible colorimetric method. It will then be necessary to carry out an extensive critical examination of the organic reagent and its color reaction. The following investigations should be made.

The Reagent. - First determine the most suitable solvent for the reagent. Frequently, water or alcohol will prove satisfactory. Then determine the solubility of the reagent and its stability in solution; i.e. whether or not it hydrolyzes, and whether or not it is affected by light, carbon dioxide, or oxygen.

The Color Reaction. - One of the first characteristics of the reaction to be determined is the effect of the hydrogen-ion concentration. Next, the stability of the colored compound should be studied. In general, if no noticeable fading occurs within twenty to thirty minutes, the reaction will be sufficiently stable for colorimetric analysis.

Other studies which must be made are listed below:¹

1. Nature of color reaction.
2. Rate of color formation.
3. Lambert-Beer law.
4. Sensitivity of the color reaction.
5. Effect of foreign ions upon the color reaction and upon its sensitivity.

1. Yoe, John H., Outline for a Detailed Investigation of a New Colorimetric Reagent (1939)

6. Effect of temperature on the color reaction over the range 15-35°C

In order to facilitate the actual testing, the solutions were grouped as given below on the basis of the reaction with certain reagents.

Group I. The original test solutions are strongly acid and are precipitated by excess of ammonia.

Al+++	Cr+++	Sn++++	Ru+++
Sb+++	Hf++++	Ta++++	CbO ₃ ⁻
Be+++	Fe+++	TiO ₃ ⁻⁻	
Bi+++	Hg ₂ ++	VO ⁺	
Ce++++	Sn++	Zr++++	

The following neutral or slightly basic solutions were included in this group simply as a matter of convenience.

CO ₃ ⁻⁻	NO ₂ ⁻	SiO ₃ ⁻⁻	S ⁻⁻
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Group II. The original test solutions are strongly acid but are not precipitated by excess of ammonia.

As+++	Ge++++	Ir++++	MoO ₄ ⁻⁻	Pd++	SeO ₄ ⁻⁻
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Group III. Aqueous solutions nearly neutral which are not precipitated in 0.1 N HCl but are precipitated in 0.1 N NH₄OH.

Cd++	Eu+++	Pb++	Pr+++	Tm+++	OsCl ₆ ⁻⁻
Co++	Gd+++	Mn++	Sm+++	Yb+++	
Dy+++	In++++	Hg++	Sc+++	Y+++	
Er+++	La+++	Nd+++	Th++++	WO ₄ ⁻⁻	

Group IV. Aqueous solutions not precipitated in either 0.1 N HCl or 0.1 N NH₄OH.

AsO ₄ ⁻⁻⁻⁻	Ca++	F ⁻	Mg++	K ⁺	Sr++	Zn++
Ba++	Cs ⁺	Ga+++	Ni++	ReO ₄ ⁻	TeO ₄ ⁻⁻	Rh+++
BO ₃ ⁻⁻⁻⁻	Cl ⁻	Li ⁺	PO ₄ ⁻⁻⁻⁻	Rb ⁺	Tl+++	
Br ⁻	Cu++	I ⁻	Pt++++	Na ⁺	UO ₂ ++	

Unclassified.

Ag ⁺	Fe ⁺⁺
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In making this arbitrary grouping, and solution of which there was any question concerning the reaction under the specified conditions was actually tested under conditions comparable to those used in the run with the organic reagent. The only difference being that a drop of 48 per cent alcohol was substituted for the alcoholic solution of the reagent. Actually, a large share of the solutions were thus tested. Furthermore, it is very difficult to make a distinct separation, as some solutions may give a partial precipitation, thus Mg^{++} and Ca^{++} were included in Group IV although they give a slight precipitate with NH_4OH .

Procedure for testing Organic Compounds.

Each organic compound is dissolved in 48 per cent ethyl alcohol, the solutions containing 50 mg. of the compound per 10 ml. of alcohol. In case the compound is not very soluble, simply use a saturated solution in 48 per cent alcohol. Ten ml. of the reagent is sufficient for all the tests.

Run No. 1

All 76 test solutions are run by simply adding one drop of the organic reagent solution to one drop of the test solution contained in a spot plate depression.

Run No. 2

Solutions of Group II are run as follows: one drop of test solution + two drops of 3 N NH_4OH + one drop of reagent solution.

Run No. 3

Solutions of Group III and IV are run as follows:

One drop of test solution + one drop of 0.3 N HCl + one drop of reagent solution.

Run No. 4

Solutions of Group IV are run as follows:

One drop of test solution † one drop of 0.3 N NH_4OH † one drop of reagent solution.

Ag^+ is run as follows:

One drop of test solution † one drop of 0.3 N NH_4OH † one drop reagent solution. Repeat the test, using one drop of 0.3 N HNO_3 in place of the 0.3 N NH_4OH .

Fe^{++} is tested according to the directions for Run 1.

Test solutions were prepared according to the methods outlined in the thesis written by B. H. Kemp, Virginia Polytechnic Institute, 1940.

In the experimental results, "Number" refers to the Virginia Polytechnic Institute number and "Source" refers to the duPont number. All of the organic compounds tested were obtained from E. I. du Pont De Nemours and Company.

Experimental Results

The following organic reagents produce no precipitates or colored solutions with the inorganic ions when tested as described in the experimental procedure.

<u>Number</u>	<u>Formula</u>	<u>Source</u>	<u>Name</u>
101-B	$C_{16}H_{14}O_4N_4S_2$	D-32-C	2-6-Di (aceto acetyl amino) m-alpha benzo thiazole (saturated solution)
102-B	$C_7H_8ClNO_3S$ (Na salt)	D-34-A	6- Chloro -2- amino toluene -3- sulfonic acid
103-B	$C_7H_8NO_3S_2Cl$	E-19-B	2- Amino -6- chloro toluene -5- sulfonic acid (saturated solution)
104-B	$C_{14}H_{11}O_3NS$	E-14-A	p- Toluene sulfonyl -p- hy- droxy benzonitrile (saturated solution)
106-B	$C_{20}H_{12}O_6NSNa$	D-32-C	1-Amino -5- phenoxy -2- aq. sulfonic acid (dark red solution)
108-B	$C_{22}H_{22}O_6SN_2$	E-4-A	Diaceto acetyl tolidene sulfone
109-B	$C_{37}H_{26}O_2Cl$	D-32-C	Isopropyl chloro di-benzan- threne
110-B	$C_{14}H_{13}O_4NS$	E-14-C	p-Toluene sulfonyl -m- hydroxy benzamide
112-B	$C_7H_8N_2O_2$	E-6-A	5-Nitro -2- amino toluene (yellow colored solution)
113-B	$C_{10}H_8O_3S$	E-3-C	B- Naphthalene sulfonic acid (free acid recrystallized)
114-B	$C_{24}H_{15}O_3N_3S_2$	E-26-C	Anthra thiasole -2- carboxy (2- (ethoxy) benzothazyl) (saturated solution)
115-B	$C_{13}H_{11}NO_2$	D-40-A	p-Hydroxy -n- phenyl phthale- mide (saturated solution)
117-B	$C_8H_{13}O_3NS$	E-7-C	1-Amino -2-4- dimethyl -6- sulfo benzene

<u>Number</u>	<u>Formula</u>	<u>Source</u>	<u>Name</u>
121-B	$C_{14}H_{11}O_3$ NS	E-14-C	p- Toluene sulfonic -m-hydroxy benzonitrile (white precipitate with water)
123-B	$C_7H_5O_4N$	D-36-A	2- Nitro benzoic acid
124-B		E-14-A	Polyvinyl Phthalimide
127-B	$C_{28}H_{22}N_4O_6S_2$	E-14-A	Di (p-toluene sulfonyl -m-hydroxy phenyl) tetrazone
128-B	$C_{16}H_{18}N_2O_2$	D-40-A	Di (p-OH) phenyl piperozene (saturated solution which is very dark brown colored and is darker in basic solutions than in acid solutions)
129-B	$C_{14}H_{10}O_3$	D-40-A	p-Hydroxy phthalide
130-B	$C_{14}H_{17}N_2O_3Cl$	D-36-B	3-Chloro -4- aceto acetylamine phenyl morpholine
131-B	$C_7H_5N_2SCL$	D-31-B	3 Chloro -1- amino benzothiazole
132-B	$C_{20}H_{32}O_4S$	D-36-C	Sulfated abistyl alcohol
133-B	$C_{14}H_{11}O_5N_3$	D-53-C	2- (4-Nitro benzoyl amine) -4-nitro toluene (saturated solution)
134-B	$C_{22}H_{24}N_2O_4$	D-54-B	Di-acetoacetyl -o- tolidine (saturated solution)
135-B	$C_{15}H_{16}N_2O$	D-54-B	6- Benzoylamine -4- amino -1-3-xylene
138-B	$C_{13}H_9NOS$	D-40-C	2-Amine thioxanthrone (saturated solution)
139-B	$C_{17}H_{15}NO$	D-40-A	7-Methoxy phenyl -b- naphthamine (saturated solution)
140-B	$C_6H_2N_3O_4F_3$	E-14-B	2-Amino -3-5- dinitro benzo trifluoride (saturated solution)
141-B	$C_{24}H_{22}O_4N_4$	D-39-C	Di-acetyl di-(p-amine phenyl) pyrazine (saturated solution)
142-B	$C_{14}H_{12}N_2O_4$	D-39-C	Di-nitro stilbene (saturated solution)

<u>Number</u>	<u>Formula</u>	<u>Source</u>	<u>Name</u>
143-B	C_7H_5OCl	D-39-C	p-Chloro benzaldehyde
144-B	C_7H_9NBrCl	D-37-A	2-Bromo -4- methyl aniline hydrochloride
145-B	$C_{14}H_8O_3$	D-39-C	Di-phenic anhydride (saturated solution)
146-B	$C_{15}H_6O_2NSCl$	E-9-B	1-9- Anthera thiazole -2- carbonyl chloride (saturated solution)
147-B	$C_7H_9NCl_2$	E-7-B	6- Chloro -2- amino toluene hydrochloride
148-B	$C_{22}H_{24}O_2S$	E-14-A	1-4- Di-butyl AQ dithiol (saturated solution)
150-B	$C_7H_{10}O_2NS$	F-2-A	p- ???? sulfonamide
151-B	$C_8H_8N_2O_5$	F-7-A	4-6- Dinitro -3- methoxy toluene (saturated solution)
153-B	$C_{14}H_6O_2Br_2$	F-7-A	1-3- Dibromo anthraquinone (saturated solution)
155-B	$C_{22}H_{18}O_2N_2$	F-6-B	1- Amino -2- methoxy-4p- toluido (saturated solution)
157-B	$C_7H_5O_6N_3$	F-6-A	3-5- Dinitro -2- amino benzoic acid (saturated solution)
158-B	$C_{20}H_{20}O_2N_4Cl_2$	F-7-A	N-N'-1-4- Phenylene bis (amino formyl methyl pyridinimo chloride)
159-B	$C_3H_6O_3$	F-5-A	Alpha trioxymethylene (no compound)
161-B	$C_9H_{12}O_2$	F-5-A	Tripropyl hydroquinone
162-B	$C_{13}H_9N_3O_6$	F-5-A	4-4'-Dinitro diphenyl amine -2- carboxolic acid (saturated solution, highly colored-yellow, slight precipitate in OH ⁻ ions)
163-B	$C_{13}H_{12}ON_2$	F-21-C	Diphenyl urea (saturated solution)
164-B	$C_6H_5O_4N_3$	F-19-B	2-6- Dinitro aniline

<u>Number</u>	<u>Formula</u>	<u>Source</u>	<u>Name</u>
165-B	$C_{20}H_{19}O_5NS$	F-21-C	2-p- Toluene sulfonamide phenyl -p- toluene sulfonate (saturated solution)
166-B	$C_{14}H_{10}O_2N_2$	F-7-B	4- Amino phenyl phthalimide (saturated solution)
168-B	$C_6H_{13}O_4SNa$	F-15-A	2- Ethyl butanol sulfate
169-B	$C_7H_8O_2N_2$	F-7-A	3-5- Diamino benzoic acid (solution is dark brown colored which turns pink in presence of H^+ ions)
170-B	$C_{12}H_9O_2N$	F-24-A	5- Nitro acenaphthene (saturated solution)
171-B	$C_{30}H_{46}O$	F-24-A	Diphenyl hepta deeryl carbinol (saturated solution)
173-B	$C_7H_7O_3N_2Br$	E-48-A	5- Benzoylamino -6- chloro 1-1'- di anthramide (saturated solution)
175-B	$C_{18}H_{17}N_3O_2$	F-13-C	4-(4'- Ethoxy phenyl) azo -1- amino -7- naphthol (saturated solution which is purplish black in color and changes to orange colored solution in OH^- ions.)
176-B	$C_9H_{14}ON$	F-13-C	2-m- Ethyl amino -4- methyl phenol (orange colored solution)
177-B	$C_{15}H_{12}O_4N_2$	F-19-C	1- Amino -6- anthraquinone car- boxylic acid NH_4 salt (saturated solution which is pink colored)
178-B	$C_{20}H_{12}O_4N_3Br$	F-19-C	1- Amino -2- bromo -4- anilido -5- nitro Aq. (saturated solution)
179-B	$C_{15}H_{12}O_4$	F-19-B	Diphenylmethone di-carboxylic acid (saturated solution which gives white precipitate in H^+ ions)
180-B	$C_{18}H_{10}O_3$	F-5-B	Bz. -1- benzanthrone carboxylic acid (saturated solution which is yellow colored but loses color in H^+ ions)

<u>Number</u>	<u>Formula</u>	<u>Source</u>	<u>Name</u>
182-B	$C_{17}H_{12}O_4S$	F-24-A	2-Methyl -1- anthraquinone thioglycollic acid (saturated solution which is orange colored)
183-B	$C_{15}H_7O_4Cl$	F-24-B	1- Chloro -2- anthraquinone carboxylic acid (saturated solution)
184-B	$C_{14}H_7O_6N$	F-25-C	2- Nitro quinizarin (saturated solution which forms a pink colored solution in OH^- ions)
185-B	$C_{14}H_4O_6N_2Cl_2$	F-25-B	1-3- Dichloro dinitro Aq. (saturated solution)
186-B	$C_{16}H_{16}O_3$	F-25-B	1-3-5-7- Tetra chloro dinitro Aq. (saturated solution which is orange colored but loses color in H^+ ions)
188-B	$C_{10}H_{13}O_2N$	F-26-C	n-Dimethyl -p- amino phenol acetate (forms a pink colored solution in OH^- ions)
189-B	$C_{15}H_7O_3Cl$	F-26-B	2- Anthraquinone carbonyl chloride (saturated solution)
191-B	$C_{20}H_{15}O_3N$	F-19-B	4'-(-2- Amino phenyl) benzoyl -2- benzoic acid (saturated solution)
192-B	$C_{21}H_{12}O_7N_2SNa_2$	F-15-C	1-NH ₂ -5-(-o- COONa aniline) Aq. -2- SO ₃ Na (saturated solu- tion which is deep red colored)
193-B	$C_{42}H_{24}O_6N_3$	F-19-B	5-Benzoylamine -1-1- dianthrimide -6'--CONHC ₆ H ₅ (saturated solution)
194-B	$C_{14}H_8O_5$	F-19-C	1-4-6- Trihydroxy Aq. (saturated solution which turns pink in presence of OH^- ions)
197-B	$C_7H_5NO_2Cl_2$	F-21-C	2-6- Dichloro -4- nitro toluene (saturated solution)
198-B	$C_{15}H_{11}O_2N$	F-21-A	1- Amino -2- methyl anthra- quinone (saturated solution)

<u>Number</u>	<u>Formula</u>	<u>Source</u>	<u>Name</u>
199-B	$C_{17}H_8OCl_2$	F-21-C	2-6- Dichloro benzanthrone (saturated solution)
200-B	$C_{18}H_{12}N_2O_2$	F-5-C	9-p- Nitro phenyl carbazol

The following organic reagents produce precipitates or colored solutions with some of the inorganic ions when tested as described in the experimental procedure. In all cases water was used as the diluent.

105-B	$C_{10}H_{10}O_2NCl$	Aceto acetyl -2- chloro aniline	D-32-C
	Run 1. Fe^{+++}	light purple colored solution, forms slowly non-fading, 5 drops dilutions.	
107-B	$C_8H_{12}O_5$	Sodium oxal acetate	E-7-A
	Run 1. Fe^{+++}	slight brown colored solution.	
111-B	$C_{10}H_{15}NO_2$	4-Chloro -2-5- diethoxy aniline	E-4-A
	Run 1. Fe^{+++}	deep lavender colored solution, forms at once, non-fading, 15 drops dilution.	
116-B	$C_9H_7O_4Cl_3$	2-Salicyl -2- hydroxy B,B,B tri-chloro ethane	D-40-B
	Run 1. Fe^{+++}	deep lavender colored solution, non-fading, forms at once, 20 drops dilution.	
	UO_2^{++}	light yellow colored solution, 10 drops dilutions.	
118-B	$C_{12}H_{15}O_3NS$	Acetoacet -o- pheni-tidine	D-36-B
	Run 1. Fe^{+++}	purple colored solution, forms at once, non-fading, 5 drops dilution.	
119-B	$C_{10}H_7N_3O_5$	1-(m-Nitro phenyl)-5- pyrazolene -3- carboxylic acid	E-7-C
	Run 1. Fe^{+++}	light greyish blue colored solution, 5 drops dilution.	
120-B	$C_9H_{10}O_3$	Benzyl glycolic acid (Na salt) (solution gives white precipitate in H^+ ions)	D-36-B
	Run 1. Cu^{++}	green precipitate, forms at once, fades slowly.	
122-B	$C_{10}H_9N_2OCl$	o- Chloro phenyl methyl pyrazolene	D-36-A
	Run 1. Fe^{+++}	orange colored solution, non-fading.	

125-B	$C_7H_9ON(HF)$	p- Amsidine hydrofluoride	E-14-A
Run 1.	Fe ⁺⁺⁺	slight pink colored solution, forms very slowly.	
	Pt ⁺⁺	slight pink colored solution, forms very slowly.	
126-B	$C_{15}H_{15}NO_4$	Furoacetyl -4- phene tidine (saturated solution which gives white percipitate in H ⁺ ions)	D-36-B
Run 1.	Fe ⁺⁺⁺	light green colored solution, non-fading, 5 drops dilution.	
	UO ₂ ⁺⁺	orange precipitate, 2 drops dilution.	
136-B	$C_{14}H_8O_3Cl_2$	Di-chloro -o- benzoyl benzoic acid (saturated solution which forms a white precipitate in H ⁺ ions)	E-26-B
Run 1.	Cu ⁺⁺	light green colored solution, forms at once, non-fading.	
137-B	$C_7H_5NS_2$	Mercapto benzo thiazole (saturated solution)	E-34-B
Run 1.	Bi ⁺⁺⁺	fine yellow colored precipitate, forms at once, non-fading, 15 drops dilution.	
	Hg ⁺	yellow colored solution, forms at once, non-fading, 10 drops dilution.	
	Pa ⁺⁺	orange colored precipitate up to about 2 ml. dilution. Orange colored solution when diluted to 50 ml., non-fading, forms at once.	
	Pb ⁺⁺	slight yellow colored precipitate, forms at once, non-fading.	
	Hg ⁺⁺	very fine white colored precipitate.	
	Cu ⁺⁺	pale green colored precipitate, non-fading, forms at once, 10 drops dilution.	
	Pt ⁺⁺	pale orange colored precipitate, slow forming, very faint color at 5 drops dilution.	
Run 2.	Pa ⁺⁺	orange colored precipitate, forms at once, shows slight color at 50 ml. dilution.	
Run 4.	Tl ⁺⁺⁺	very fine yellow colored precipitate, non-fading.	
	Zn ⁺⁺	very fine white colored precipitate, slow forming, non-fading.	
149-B	$C_{11}H_{14}O_2S$	Benzyl thio (AA)	D-??-D
Run 1.	In ⁺⁺⁺	slight white colored precipitate, forms at once, non-fading, 5 drops dilution.	

Pb⁺⁺ slight white colored precipitate, forms at once, 5 drops dilution.
Sc⁺⁺⁺ slight white colored precipitate, forms at once, 5 drops dilution.
Ga⁺⁺⁺ slight white colored precipitate, forms at once, 5 drops dilution.
Cu⁺⁺ greenish white colored precipitate, forms very slowly.

152-B C₃H₅OS₂K Potassium xanthate F-11-C

Run 1. Bi⁺⁺ yellow colored solution, forms at once, non-fading, 25 drops dilution.
Fe⁺⁺⁺ dark brown colored precipitate, forms once, non-fading, 25 drops dilution.
Hg⁺ black colored precipitate, forms at once, very slight color at 10 drops dilution.
Sn⁺⁺ yellow colored solution, forms at once, fades slowly, 25 drops dilution.
Co⁺⁺ green colored precipitate, forms at once, non-fading, 25 drops dilution.
Pb⁺⁺ light green colored solution, forms at once.
MoO₄⁻⁻ deep lavender colored precipitate, at 5 ml. dilution there is a faint pink colored solution.
Ni⁺⁺ brown colored precipitate, forms at once 5 ml. dilution.
Cu⁺⁺ yellow colored precipitate, forms at once, 15 ml. dilution.
Ag⁺ in basic and acid solutions gives a yellow colored precipitate, 5 drops dilution.
In⁺⁺⁺ white colored precipitate, forms at once, 15 drops dilution.
Pd⁺⁺ yellow colored precipitate, non-fading, forms at once, 20 drops dilution.
Pt⁺⁺ yellow colored precipitate, 15 drops dilution.
Ir⁺⁺⁺⁺ reagent takes the color of the IrCl₆⁻⁻ ion out at once.
Cb⁺⁺⁺⁺ green colored solution, forms at once, 5 drops dilution.
Run 2. Pd⁺⁺ yellow colored precipitate, forms at once, non-fading, 20 drops dilution.
Run 3. Co⁺⁺ greenish colored precipitate, non-fading, forms at once, 15 drops dilution.
Ni⁺⁺ dark brown colored precipitate, non-fading, forms at once, turns to a pink colored solution at 15 ml. dilution

	Cu ⁺⁺	yellow colored precipitate, non-fading, forms at once, 15 ml. dilution.	
Run 4.	Ni ⁺⁺ Cu ⁺⁺	brown colored precipitate, forms at once. yellow colored solution, non-fading 15 ml. dilution.	
154-B	C ₆ H ₇ ON	p- Amino phenol (saturated solution which is deep greyish colored in OH ⁻ ions and turns to a purple colored solution on standing)	F-9-B
Run 1.	Ce ⁺⁺⁺	very light brown colored precipitate, forms slowly, non-fading.	
	Fe ⁺⁺⁺	deep lavender colored precipitate, forms at once, 25 ml. dilution.	
	Hg ⁺	very very light blue colored precipitate.	
	Ru ⁺⁺	brown colored precipitate, difficult to make distinction between it and color of the Ru ⁺⁺ ion.	
	Cb ⁺⁺⁺⁺	blue colored precipitate, slow forming.	
	CO ₃ ⁻⁻	dark brown colored precipitate which is probably due to basicity of the test solution.	
	S ⁻⁻	dark brown colored precipitate, forms slowly.	
	Dy ⁺⁺⁺	brown colored precipitate, forms slowly.	
	Pb ⁺⁺	light brown colored precipitate, forms slowly.	
	Hg ⁺⁺	dark brown colored precipitate, forms at once, non-fading, 10 drops dilution	
	Tm ⁺⁺⁺	light brown colored precipitate, slow forming.	
	Cu ⁺⁺	heavy dark black precipitate, forms at once, 25 ml. dilution if let stand about 5 minutes.	
	Pt ⁺⁺	purple colored solution, forms slowly.	
	Ir ⁺⁺⁺	black colored precipitate, forms slowly, 5 drops dilution.	
Runs 2, 4.	Ni ⁺⁺	blue colored precipitate, forms slowly, colored solution in all due to the effect on OH ⁻ ions on the reagent.	
156-B	C ₃₀ H ₂₄ O ₄ N ₂	B.O.N. of moho furoyl toluidine (saturated solution)	F-7-B
Runs 1.	Fe ⁺⁺⁺	yellow colored solution, very slow forming, 10 drops dilution.	
160-B	C ₄ H ₁₀ ON ₂	Di-methyl glycineamide	F-7-A
Run 1.	Fe ⁺⁺⁺	orange colored precipitate, non-fading, 10 drops dilution.	

	Cu ⁺⁺	purple colored solution, forms at once, 15 drops dilution.	
Run 4.	Cu ⁺⁺	purple colored solution, forms at once, non-fading, 15 drops dilution.	
167-B	C ₁₃ H ₁₁ O ₂ N	4(4' Amino phenoxy) benzaldehyde (saturated solution which is brown colored)	F-7-B
Run 1.	Fe ⁺⁺⁺	slight pink colored solution, slow forming.	
	Cu ⁺⁺	slight yellow green colored precipitate, forms very slowly.	
172-B		Di-Cp nitro benzyl 3 (?) toluidine (saturated solution)	E-48-C
Run 1.	Fe ⁺⁺⁺	yellow colored solution, forms at once, 1 ml. dilution.	
181-B	C ₅ H ₉ O ₃	Furoic acid	F-26-A
Run 1.	Fe ⁺⁺⁺	light yellow colored solution.	
190-B	C ₁₆ H ₂₀ O ₂ N ₆	4-4- Diguanidine -3-3'-dimethoxy biphenyl di HCl	F-21-C
Run 1.	Ir ⁺⁺⁺	pink colored solution which fades to a brown colored solution very very quickly. This solution after standing a few minutes produces a brown colored precipitate. 10 drops dilution.	
195-B	C ₇ H ₇ O ₂ N	5-Amino -2- hydroxy benzaldehyde (saturated solution which forms a brown colored solution in OH ⁻ ions)	F-19-B
Run 1.	S ⁻⁻	slight pink colored solution.	
	Fe ⁺⁺⁺	slight pink colored solution, forms slowly.	
196-B	C ₁₀ H ₉ ON	2-5-Amino naphthol (saturated solution)	F-21-C
Run 1.	Fe ⁺⁺⁺	slight brown colored solution, forms slowly.	
Run 4.	Cu ⁺⁺	heavy purple colored precipitate, forms at once, 20 drops dilution.	

DISCUSSION OF RESULTS

It is fully realized that only 100 organic compounds are but a beginning in the large field of the search for new organic compounds as colorimetric reagents for inorganic ions and only plays a small part in the assimilation of data which may help to predict color reaction with certain types of organic compounds. It is hoped that the results obtained may be some value towards this end, but no definite conclusions can be drawn from such a limited study. Of the 100 organic compounds tested twenty-four gave colored solutions or precipitates. Fe^{+3} was the most reactive of the seventy-six metallic and non-metallic ions tested, giving a precipitate or colored solution with eighteen of the compounds.

Only two of the organic reagents tested showed possibilities of being developed into colorimetric reagents, namely, 137-B, mercapto benzo thiazole as a reagent for the Pd^{+2} ion and, 190-B, 4-4' diguanidine -3-3'- dimethoxy biphenyl di HCl as a reagent for the IrCl_6^{--} ion. 137-B shows possibilities in that one part of Pd^{+2} in a million parts of water can be detected with the naked eye, but a reagent for the Pd^{+2} ion has been recently studied by Yoe and Overholser¹ which is sensitive to 1 part in 300,000,000. 190-B shows possibilities in that the IrCl_6^{--} ion is the only ion with which this compound reacts.

1. Yoe, J. H. and Overholser, L. G., J. Am. Chem. Soc., 61, 2058 (1939)

The other reagents which gave color reactions had one or more of the following disadvantages of being developed into colorimetric reagents; the reaction was not sensitive enough, the color due to the reaction fades too quickly, or the compound reacts with so many different ions as to be of little selective importance.

PART II

A STUDY OF THE REACTION BETWEEN 2 ACETAMINO
6 AMINO BENZO THIAZOLE AND CHLOROIRIDIC ACID

HISTORICAL

In Mendeleeff's table, Group VIII was distinctive from the fact that in place of a single element in each series there were blanks in all series except the fourth, sixth, and tenth, and these spaces were occupied by triads, which show some striking analogies. Not only do the members of each triad show closely related properties, but their atomic weights and atomic volumes are much closer together than usual in successive elements. This similarity is not only true of physical properties but it is so strikingly true of the chemical properties that the separation of each of these triads are among the more difficult operations of analytical chemistry.

In addition to the resemblance within the triads themselves, there is also a certain similarity between each element and the corresponding element in the other triads. Thus iron, ruthenium, and osmium have certain peculiar properties in common; cobalt, rhodium, and iridium are somewhat alike; and nickel, palladium, and platinum present similar peculiarities.

The resemblances in these vertical triads are especially striking between the last two members but it is perhaps to be expected that the first member of such a group would differ somewhat from the other members.

The principal physical properties as given by Hopkins¹ are shown in the following table.

1. Hopkins, B. S., "Chemistry of the Rarer Elements," (D. C. Heath & Co., New York, 1923) p. 338

Physical Properties of the Platinum Metals

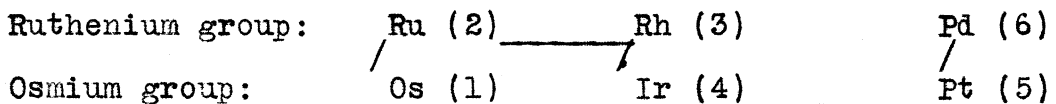
	Atomic Weight	Mean Atomic Heat	Melting Point C°	Boiling Point C°	Density
Iron	55.84	6.64	1505	2450	7.84
Cobalt	58.97	6.34	1489	2415	8.8
Nickel	58.68	6.40	1452	2340	8.3-8.8
Ruthenium	101.7	6.21	1950	2520	12
Rhodium	102.9	5.97	1940	2500	11-12
Palladium	106.7	6.30	1542	2540	11.4-12
Osmium	190.9	5.94	2700	----	21.3-24
Iridium	193.1	6.24	2360	2440	22.4
Platinum	195.2	6.31	1755	3900	20.9-21.7

It is to be observed that there are close resemblances within the triads, although there is considerable departure from the order of atomic weights. Among the notable facts to be observed are the high melting points, boiling points and high density of osmium, iridium, and platinum.

The metals of this group are all white and remain untarnished in dry air. Iron is unique in that it oxidizes readily in moist air, while the other metals either tarnish superficially or are entirely unchanged. The metals, especially in colloidal form or in finely divided state, are the best catalysts known. All the metals form organo-metallic compounds, a fact which contrasts them with the other members of the even series. There is also a marked tendency to form complex radicals, both basic and acidic, from which extended series of compounds are derived, the properties of which are entirely different from the properties of the corresponding metallic salts.

The rare elements; ruthenium, rhodium, palladium, osmium, iridium, and platinum are commonly called the "platinum metals" because they occur together in native platinum, from which they were first isolated. They fall into two distinct sub-groups, viz. the lighter platinum metals (ruthenium group), and the heavier platinum metals (osmium group). Again, they may be grouped in three pairs according to their vertical arrangement in the Table. The members of each pair have certain features in common, although the six metals resemble each other in some respects.

Perhaps the most gradual transition in chemical deportment may be observed if they are placed in the order indicated below:--



or Os--Ru--Rh--Ir--Pt--Pd

About the year 1803, several chemists examined the residue which remains as a black powder when platinum is dissolved. This had always been considered to be composed mainly of plumbago, but it was found to contain a new metal. In 1804 Tennant¹ announced the discovery of two new metals from this residue. For one he suggested the name "iridium", the rainbow element, "from the striking variety of colors which it gives while dissolving in acid." The other he name "osmium", from the Greek work meaning odor.

The metal, iridium, is white, with a bluish luster, resembling polished steel in appearance. As usually obtained, it

1. Hopkins, B. S., "Chem. of the Rarer Elements," (D. C. Heath & Co., New York, 1933) p. 342

is hard, brittle, and almost entirely lacking in ductility. It has been both melted and vaporized¹ in the electric furnace. All simple acids and even aqua regia are without action on the metal except in very finely divided state or in alloys, in which condition a slow partial solution takes place.

Iridium can be determined qualitatively by treating the unknown with an oxidizing agent so that if iridium is present it will be in the tetravalent condition. The solution is then treated with an excess of alkali hydroxide, this gives a green solution with a small black precipitate of the double chloride. On heating the solution it first becomes red, then deep azure blue, due to the precipitation of $\text{Ir}(\text{OH})_4$. This test is one of the most useful in determining iridium as it very clearly distinguishes iridium from platinum.²

Woo and Yost³ determined iridium quantitatively in two ways and the results compared very favorably. One method was by reducing a solution of chloroiridate to chloroiridite with KI and titrating the liberated I_2 with $\text{Na}_2\text{S}_2\text{O}_3$, the other was estimating the amount of iridium with titanous chloride and determining the end-point electrometrically.


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1. Hopkins, B. S., "Chem. of the Rarer Elements," (D.C. Heath & Co., New York, 1923) p. 352.
 2. Hopkins, B. S., *ibid.*, p. 366.
 3. Woo, Sho-Chow and Yost, D. M., J. Am. Chem. Soc., 53, 884-8 (1931)

THEORETICAL

From the standpoint of structure¹, there are two fundamental requirements for a good organic analytical reagent. First, with the exception of a few coordinating compounds, they must contain an acid or salt-forming group in order to react with a metallic ion. The most important of these are: (1) the amino, or = NH group; (2) the oxime, or = NOH group; (3) the hydroxyl, or - OH group, and (4) the mercapto, or - SH group. The carboxyl, or - COOH group, and the sulfonic, or - SO₃H group, have been of little importance so far, although they have been used.

The second fundamental requirement is that the molecular structure of the reagent be such as to make possible the formation of a ring containing the metal², usually by means of one electrovalence link and one coordinate valence, although this is not absolutely necessary, and either two electron valences or two coordinate valences may be employed.

The metal is almost always attached to a nitrogen, sulfur, or oxygen atom and very rarely attached to a carbon atom.

The structural formula for 2 acetamido 6 amino benzo thiazole is  and the type or structure of the compound formed when this reacts with chloroiridic acid is not known.

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1. Sarver, L. A., J. Chem. Educ., 13, 511-4 (1936)
 2. Sidgwich, N.V., "The Elect. Theory of Valence", Oxford, (1927)

EXPERIMENTAL RESULTS

The melting point of 2 acetamino 6 amino benzo thiazole as received from Dr. John H. Yoe, of the University of Virginia, was determined. The compound decomposed at 247° C when heated rapidly and when heated slowly decomposed at 233° C. The compound was purified by recrystallization from a 48 per cent solution of ethyl alcohol. The compound after the first recrystallization decomposed at 225° C and after the second recrystallization it decomposed at 223° C.

The reaction between 2 acetamino 6 amino benzo thiazole and chloroiridic acid produced a purple brownish color which changed to a purple brownish precipitate after standing a few minutes. The color of the solution produced was lighter in color than the color of the iridium^{III} ion itself. The same color reaction was obtained between iridium and reagent whether the reagent as received, after the first recrystallization, or after the second recrystallization was used indicating that the compound as received was of a high degree of purity.

Comparisons were made (using 100 ml. Nessler tubes with a Nesslerimeter) between distilled water, solutions of $\text{H}_2\text{IrCl}_6^+$ organic reagent, and solutions of H_2IrCl_6 . By use of the Nesslerimeter it was possible to detect a very slight difference in the color intensity of distilled water and a solution containing 0.15 mg. of Ir^{+4} and 0.3 mg. of reagent per 100 ml. of solution but this solution had the same color intensity as a solution containing

only 0.05 mg. of Ir^{+4} per 100 ml. of solution. This is a ratio of approximately one mole of Ir^{+4} to two and one-half moles of reagent. Comparisons were made increasing the ratio of the reagent up to as much as ten to one but this had no effect on the color intensity of the reaction.

In the reaction between the reagent and chloroirdic acid there was no detectable difference in the color of the reaction when the quantity of Ir^{+4} was increased by as much as 0.1 mg. per 100 ml. of solution (an excess of reagent being used in all cases).

Solutions of a pH of 2.2, 3.0, 4.0, 5.0, and 6.0 were made according to the directions as given by Clark¹ and these were checked with antimony electrodes using a Thwing-Albert pH meter and checked to within ± 0.2 units. Solutions were made up using different concentrations of Ir^{+4} + reagent + buffers of the above pH and no differences in the color intensity of the solutions could be detected by varying the pH. The pH did not seem to effect the reaction provided the solution was acid. The color reaction did not take place in basic solutions.

The original purpose of this investigation was to try to develop this organic compound as a definite quantitative colorimetric reagent for the detection and determination of iridium but from the above results it was found that the reaction was not sensitive enough for this and then the problem developed into one of qualitative nature.

1. Clark, W. M., "The Det. of Hydrogen Ions", (Williams and Wilkins Co., Baltimore, 1920) p. 69-72.

There are ions that react with 2 acetamino 6 amino benzo thiazole other than iridium anion, namely, ferric iron, palladium, and ruthenium.

Palladium produces a yellow precipitate in concentrated solution (one mg. per ml.) and in more dilute solutions (0.2 per ml.) produces a faint yellow colored solution with 2 acetamino 6 amino benzo thiazole. Both ferric iron and ruthenium produced a dark brown colored precipitate which is very similar to the precipitate produced by chloroiridic acid with the reagent. When palladium and chloroiridic acid were together in solution, the palladium ion did not interfere with the test for iridium anion provided iridium was present in as much as 0.5 mg. per ml. of solution.

Ruthenium ions are so highly colored that it was difficult to detect the precipitate formed after the addition of the reagent but by letting it stand a few minutes the dark brown precipitate showed up. When the precipitates from solutions of chloroiridic acid + reagent, ruthenium + reagent, and chloroiridic acid + reagent were compared there was no detectable difference to be noted.

The problem then was to separate ruthenium and iridium. Ruthenium may be precipitated as a black precipitate with NH_4OH but iridium can not be precipitated with NH_4OH . A separation based on this fact was attempted. Solutions of iridium and ruthenium chlorides were treated with NH_4OH and the precipitate separated. The filtrate was made acid with HCl and the organic reagent added but no positive test for

the iridium anion could be detected. (By "test", it is meant that no color or precipitate was formed.) Other solutions from which the ruthenium was precipitated by means of NH_4OH were treated with HCl and concentrated down to a small volume and still no test for the iridium anion could be noticed. Other solutions were taken to dryness before the HCl was added, the residue taken up in HCl and no test for the iridium anion was detected.

A method¹ of separating ruthenium and iridium as given by Schoeller and Powell was tried and found successful. A solution of iridium and ruthenium chlorides was treated with potassium carbonate and potassium nitrite and heated until the solution lost its green color. The solution was then evaporated to dryness and the residue treated with alcohol which dissolves the ruthenium but not the iridium. The residue after the alcohol treatment, was taken up in HCl and the organic reagent added. A purple brownish precipitate formed slowly. Other solutions which contained ruthenium and other ions (any except ferric iron) other than the iridium anion were treated in a similar manner and no colored solution or precipitate formed.

Ferric iron produced a precipitate with the organic reagent which was very similar to the precipitate produced by chloroiridic acid. Ferric iron must be removed, if present, before any positive test for the iridium anion can be established or confirmed. This separation was tried in several ways but all proved unsuccessful. A solution of ferric nitrate and

- 1. Schoeller, W. R., and Powell, A. R., "The Anal. of Minerals and Ores of the Rarer Elem.", (Charles Griffin & Co. London, 1919) p. 199

chloroiridic acid were treated with NH_4OH and the ferric hydroxide filtered off. The filtrate was then treated with HCl and the organic reagent added but no colored solution or precipitates formed.

Ferrous iron does not give a colored solution or precipitate with the organic reagent and neither does the trivalent form of iridium. This limits the possibilities of using reducing agents to reduce the ferric iron, as tetravalent iridium is also easily reduced to the trivalent form.

A solution of chloroiridic acid was treated with sulfuric acid and the solution gently boiled to produce iridium sulfate. To this solution the organic reagent was added and no colored solution or precipitate formed.

Solutions of chloroiridic acid were made alkaline with NH_4OH and then made acid with HCl and the resulting solution did not give a colored solution or precipitate with the reagent. Solutions of chloroiridic acid after being made alkaline with NH_4OH were evaporated to dryness and the residue taken up in dilute KOH and then made acid with HCl and still no colored solution or precipitate formed with the organic reagent. It was thought that possibly the tetravalent iridium had been reduced when treated with NH_4OH so the solution was oxidized with chlorine after being made acid with HCl and still no test for the iridium anion could be confirmed.

DISCUSSION OF RESULTS

It was hoped that 2 acetamino 6 amino benzo thiazole could be developed into a quantitative colorimetric reagent for the determination of iridium but the color produced by the reaction was not as strong as the color of the iridium anion (IrCl_6) itself. The iridium anion is so dark that it is difficult to detect a great difference in its color and the color produced in the reaction between reagent and chloroiridic acid. The reaction between the reagent and chloroiridic acid was not sensitive enough and there was not enough difference in color produced by a small increase in the concentration of iridium to be of importance quantitatively.

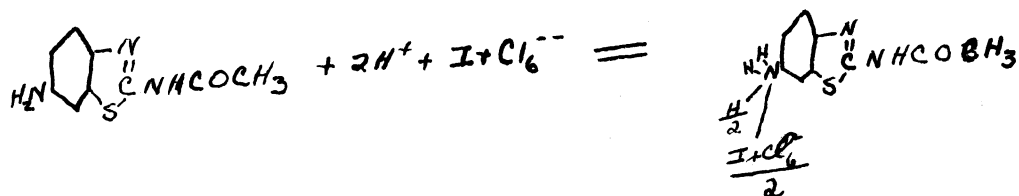
The pH of the solution had no effect on the color intensity of the reaction provided the solution was acid. The color reaction did not take place in basic media.

Ruthenium and ferric iron interfered with the color reaction between reagent and chloroiridic acid. Both produced by the iridium anion. Ruthenium may be separated satisfactorily but no method of separating iron from iridium was accomplished.

Whenever a solution of chloroiridic acid was made alkaline with NH_4OH and again made acid with HCl no color or precipitate was formed when the organic reagent was added. The reason for this was not determined.

H_2IrCl_6 ionizes into $2\text{H}^+ + \text{IrCl}_6^{--}$ and it is possible and

probable that the following addition takes place with 2 acetamino 6 amino benzo thiazole.



CONCLUSIONS

The reaction between 2 acetamino 6 amino benzo thiazole and chloroiridic acid is not sensitive enough to be of importance as a colorimetric quantitative reaction.

IrCl_6^{--} can be detected with this organic compound if iridium is present in as much as 0.02 mg. per ml. of solution providing ferric iron is absent. If ruthenium is present it must be removed before the test for the iridium anion can be made.