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The Detection of Poisons

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THE DETECTION OF POISONS.

Submitted in fulfillment of the requirements for honors
in the Department of Chemistry in Ursinus College.

May 16, 1913.

Lloyd S. Cassel.

THE DETECTION OF POISONS.

Toxicology is one of the most comprehensive of the sciences and may be defined as that branch of medical science which treats of poisons. It is not easy to define the term poison but it may be defined or considered as any substance, which, acting chemically or physiologically, uniformly causes deleterious effects or death, when brought in contact with, introduced into or generated within the body.

The parts of the body usually examined in the case of suspected poisoning are the stomach and contents, the intestines and contents, the liver, the kidneys, the brain, muscular tissue, the bladder and a portion of urine. The organic material should be ground or chopped and distilled under proper conditions.

Phosphorus, alcohol, chloroform, hydrocyanic acid, carbolic acid, aniline, nitrobenzene, etc., may be separated from organic admixture by distillation. The contents of the stomach, intestine and finely divided viscera should be acidulated with Tartaric acid prior to distillation.

The alkaloids, many glucosides and bitter principles, as well as certain synthetic drugs like acetanilide, phenacetine and anti-pyrine are not volatile and must be extracted from extraneous matter with hot alcohol containing tartaric acid.

Arsenic may be separated from organic matter by drying the organic substance and distilling with strong hydrochloric acid and potassium chlorate. Other metallic poisons should be tested for directly in the presence of the organic matter or after its destruction by proper oxidizing agents.

Yellow Phosphorus, Hydrocyanic Acid, Carboic Acid, Chloroform, Chloral Hydrate, Nitrobenzene, Aniline, Ethyl Alcohol, Acetone and Carbon Disulphide are among the most important volatile poisons.

Phosphorus can be detected with certainty by either the Mitscherlich or the Blondlot-Dussard test. Free Phosphorus may be detected by Scherer's test. This test is based on the reducing action of Phosphorus vapor on a solution of silver nitrate which becomes blackened if exposed to its action. Some of the original material was placed in a small Erlenmeyer flask. A small quantity of ether was added and a strip of white filter paper, moistened with silver nitrate solution, was suspended in the mouth of the flask. The fact that the filter paper was darkened proved the presence of Yellow Phosphorus.

The most delicate test for the detection of P is based on the luminosity of its vapor. This is known as the Mitscherlich method and was carried out as follows:

The matter under examination was placed in a large flask and equal volumes of water and H_2SO_4 were added. The flask was then adjusted to a Liebig condenser. The application of heat vaporized the phosphorus and observations made in the dark showed flashes of light and even a luminous ring at the point of condensation. When much P is present the tube will be luminous throughout its whole extent. One part of phosphorus in 200,000,000 parts of substance has been detected by this method.

The Blondlot-Dussard method is based on the fact that phosphine burns with a beautiful green flame which can easily be seen in a dark room. The test was carried out as follows:

Some of the original material was placed in a hydrogen generating

flask and the gas was passed through AgNO_3 solution for several hours. The black precipitate of silver phosphide was collected on a filter free from ash. Hydrogen was generated from phosphorus-free Zn and H_2SO_4 . The black precipitate of silver phosphide was washed into a flask and phosphorus was tested for. A green cone appeared upon the hydrogen flame and a porcelain dish depressed upon the flame produced a beautiful emerald-green glow.

Chronic phosphorus poisoning is especially liable to occur among people engaged in the manufacture of phosphorus matches. " Phossy " jaw is caused by the inhalation of phosphine. Many States have passed laws requiring the use of Phosphorus trisulphide in the making of matches. This compound has no deleterious effects.

Hydrocyanic Acid, HCN , is a very powerful poison which can easily be recognized by its odor.

The following tests were applied for the detection of Hydrocyanic Acid.

(1) A portion of the distillate was acidified with dilute Nitric Acid, and a solution of silver nitrate was added. A white curdy precipitate of AgCN ^{was formed}. The limit of delicacy is 1:250,000.

(2) Prussian Blue Test. A solution of KOH was added to the distillate, one or two drops of ferrous sulphate and one drop of ferric chloride solution. The mixture was warmed and then acidulated with dilute HCl. A precipitate of Prussian Blue was formed.

(3) Sulpho - Cyanate Test. Three or four drops of KOH solution were added to a portion of the distillate. Then a small quantity of Ammonium Sulphide. The solution was evaporated to dryness, the residue dissolved in water acidified with dilute HCl. The solution was filtered to remove sulphur and a drop of ferric chloride was added. A reddish to blood-red color appeared.

Quantitative Determination of HCN.

A weighed portion of material was acidified with tartaric acid and distilled.

AgCn was precipitated from silver nitrate solution. The precipitate was ignited in a weighed porcelain crucible. The quantity of metallic silver obtained was then determined.

Calculations according to my quantitative findings:

Weight of Ag No ₃	0.309 grams.
" " crucible and Ag Cn.....	37.7265 gr.
" " " alone.....	37.4850.
" " Ag Cn.....	0.2415.

Factor:

Ag CN(134): Ag(108) = 0.8059
 0.2415 x 0.8059 = 0.194625

Weight of crucible, Ag Cn, ash and reduced Ag.....	37.7303 gr,
" " " and Ag Cn.....	37.7265 gr.
" " ash0002 gr.
	<u>337.7263</u>
	0.0040 gr,

Total Silver:-

0.194625 plus 0.004 = 0.198625
 $\frac{0.198625 \times 100}{0.309} = 64.28 \% \text{ of Ag.}$

Formula Weight of Ag₂NO₃ = 169.66
 " " " Ag = 108.

$\frac{108 \times 100}{169.66} = 63.45 \%$

Calculated percentage of Ag.....	64.28
Theoretical percentage	63.45
Error of Calculation	0.83 %

Carbolic Acid, C₆H₅.OH, is one of the most deadly and rapidly acting poisons known. The odor is very characteristic and is one of the most delicate tests for Carbolic Acid.

The tests enumerated below were made for Carbolic Acid:

(1) Millon's Test.- Millon's Reagent (1 part of Hg dissolved in 1 part of fuming Nitric Acid) heated with a solution containing only a trace of Phenol struck a red to dark-red color. A distinct red color is given by 0.00005 grams of Carbolic Acid diluted 1:100,000.

(2) Bromine Water Test.- This reagent produced a yellowish- white precipitate of tribromophenol (C₆H₂.Br₃.OH) even with a very dilute solution of the acid.

(3) Ferric Chloride Test.- A solution of Fe Cl_2 gave a violet or purple color with an aqueous Phenol solution.

Quantitative Determination of Carbohic Acid.

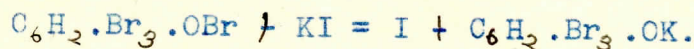
The calculations according to my quantitative findings were based on those of the Koppeschaar-Beckurts method as given in " The Detection of Poisons " by Autenrieth and Warren.

The following standard solutions are required:

- (1) N/100 Potassium Bromide solution containing 5.939 grams per 1000 C.C.
- (2) N/100 Potassium Bromate solution containing 1.667 grams per 1000 c.c.
- (3) N/10 Sodium Hyposulphite solution containing 24.83 grams per 1000 c.c.
- (4) Potassium Iodide solution containing 125 grams of KI per 1000 c.c.

The method of procedure was as follows:

25 c.c. of 0.1 per cent carbohic acid solution were put into a tightly stoppered flask. 50 c.c. each of standard KBr and KBrO_3 solutions were added, then 5 c.c. of pure, concentrated sulphuric acid were added and the mixture was shaken vigorously. The flask was opened in 15 minutes and 10 c.c. of standard KI solution were added. After five minutes free iodine was titrated with N/10 sodium hyposulphite solution. Excess of free bromine and also precipitated tribromophenol bromide acted upon the KI, according to the equation:



Each molecule of carbohic acid required 6 atoms of bromine which in turn set 6 atoms of iodine free.

The calculation according to my quantitative findings being:

Sulphuric acid liberates 0.1994 grams of bromine from 50 c.c. of N/100 KBr solution, and 0.0399 grams from 50 c.c. of N/100 KBrO_3 solution, or 0.2393 grams in all.

Since each molecule of carbohic acid requires 6 atoms of bromine, the following proportion shows how much carbohic acid can be converted

into tribromophenol by 0.2393 grams of bromine:

$$\begin{array}{l} 6 \text{ Br: } \text{C}_6\text{H}_3\text{OH} \\ 480 \quad 94 \quad = 0.2393 : x, \\ \text{and } x = 0.0469 \text{ grams.} \end{array}$$

1 c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ solution corresponds to 0.008 grams of bromine which can convert 0.00156 grams of carboic acid into tribromophenol, for

$$480 : 94 = 0.008 : x,$$

and $x = 0.00156$ grams. Therefore, for every c.c. of N/10 sodium hypsulphite solution, used to combine with iodine set free by bromine, subtract 0.00156 grams from 0.0469 grams of carboic acid.

Chloroform, CHCl_3 , is easily recognized in the free state by its characteristic odor. It separated from the distillate in heavy, colorless globules.

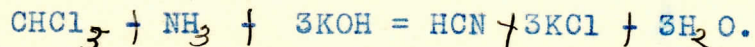
The following tests were made in the detection of chloroform:

(1) Phenylisocyanide Test.-On the addition of a few drops of aniline and an alcoholic solution of KOH to the distillate Phenylisocyanide was formed. The penetrating and repulsive odor of this compound was easily recognized.

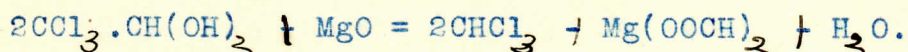


Fehling's Solution Test.- A red precipitate of cuprous oxide was formed upon warming the distillate with Fehling's solution.

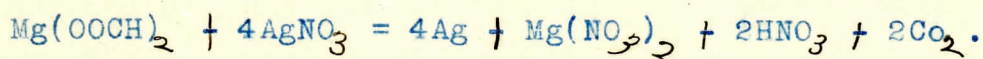
(3) Conversion of chloroform into HCN.- A portion of the distillate was put into a pressure flask with some solid ammonium chloride and 2 c.c. of alcoholic KOH solution. The flask was sealed and heated to boiling in a water-bath. The solution was cooled and the Prussian Blue test for HCN was made.



Chloral Hydrate, $\text{CCl}_3\text{.CH(OH)}_2$, produces pronounced coma when taken internally. Reducing agents reduce it to Chloroform. Heating it with calcined magnesium oxide reduced it to chloroform and formic acid.



Mercuric chloride solution formed white, mercurous chloride (Hg_2Cl_2) with formic acid. Upon warming with silver nitrate solution metallic silver was deposited by the action of the formic acid.



Tests as enumerated below were made for chloral hydrate.

(1) The addition of Nessler's reagent to an aqueous chloral hydrate solution produced a brick-red precipitate which in time changed to a dirty yellowish-green.

(2) When a few c.c. of chloral hydrate solution were boiled with a small quantity of sodium hyposulphite solution and KOH solution a turbid liquid with a brick-red color was formed.

Iodoform, CHI_3 , may be recognized by its distinctive odor. Upon gently warming a few drops of alcoholic iodoform solution with a small quantity of sodium phenolate ($\text{C}_6\text{H}_5\text{.ONa}$) solution a red substance was precipitated.

Nitrobenzene, $\text{C}_6\text{H}_5\text{.NO}_2$, was detected by its odor and by the separation of yellowish globules in the distillate.

(1) The addition of a few drops of an aqueous solution of sodium hypochlorite produced a violet-blue or purple-violet coloration which gradually changed to a dirty red.

(2) Bromine water produced a flesh-colored precipitate when added to an aqueous solution of aniline. This test is very sensitive 1 : 66,000.

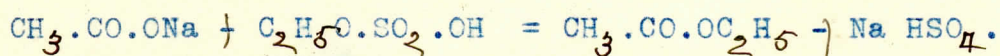
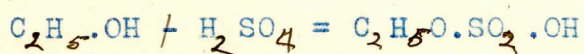
Aniline, $\text{C}_6\text{H}_5\text{.NH}_2$, was detected by tests 1 and 2 described under Nitrobenzene.

Ethyl Alcohol, $C_2H_5.OH$, affects the brain very materially. It was recognized by its odor and by the following tests:

(1) Berthelot's Test.- The distillate was shaken with a few drops of benzoyl chloride and 3 to 5 drops of NaOH. Ethyl benzoate which has a characteristic, aromatic odor was formed.



(2) Ethyl Acetate Test.- The liquid containing alcohol was mixed with the same volume of sulphuric acid and ~~and~~ a small quantity of sodium acetate was added.



Ethyl Acetate was easily recognized by its odor.

Acetone, $CH_3.CO.CH_3$, is not poisonous. The following tests were made for it:

(1) Lieben's iodoform test.- Yellowish crystals of iodoform were formed upon the addition of a few crystals of iodine and a small quantity of KOH solution to the distillate.

(2) Legal's Test.- The addition of sodium nitroprusside solution and KOH solution to the liquid containing acetone produced a red or ~~yellowish~~ ~~red~~ reddish-yellow color which soon changed to yellow. The addition of Acetic acid in excess changed the color of the solution to carmine or purplish-red. Heat changed the color to violet.

Carbon Disulphide, CS_2 , is a colorless liquid having a very characteristic odor. Taken internally, it causes decomposition of the red blood-corpuses.

CS_2 was detected by the following tests:

(1) Lead Acetate Test.- Lead Acetate and KOH solutions caused a black precipitate of PbS when added to the aqueous carbon disulphide solution.

(2) Sulphocyanate test.- The distillate was heated with ammonium hydroxide solution and alcohol. The addition of ferric chloride solution caused

a deep red color to be formed.

(3) Xanthogenate Test.- A few c.c. of the distillate were shaken with excess of a saturated solution of KOH in absolute alcohol. The solution was acidified with acetic acid and 1 or 2 drops of copper sulphate solution were added. A brownish-black precipitate of cupric xanthogenate was formed.

NON-VOLATILE ORGANIC SUBSTANCES.

The alkaloids and glucosides are not volatile with steam and must, therefore, be extracted from the organic matter by the "Staas-Otto" method.

The matter to be examined was mixed with absolute alcohol and then acidulated with tartaric acid. The flask was connected with a reflux condenser and heat was applied. The mixture was cooled and filtered. The filtrate was evaporated to a syrup in a small glass dish on the water bath. The residue was mixed with 100c.c. of water, filtered and evaporated again. The residue was mixed with absolute alcohol and then filtered. The solution was evaporated and the residue was dissolved in 50c.c. of water. The acid, aqueous solution was then extracted 2 or 3 times with ether. The ether solution was slowly evaporated in a small glass dish upon a water-bath previously heated slightly above 35 degrees. Precautions were taken not to have gas burning during this operation. The residue was examined for Acetanilide, Phenacetine, Picric Acid, Caffeine, Antipyrine and Salicylic Acid.

Picric Acid, $C_6H_2(NO_2)_3.OH$ is an intense yellow, crystalline substance which was recognized by the following tests:

(1) Dyeing Test.- The substance containing the Picric Acid was dissolved in hot water. A woolen and a cotton thread were then introduced into this solution. About twelve hours later the threads were removed and rinsed in pure water. The fact that the woolen thread was colored yellow proved the presence of picric acid.

Picric acid is not fast upon vegetable matter like cotton. Picric acid diluted 1:110,000 will produce a yellow color on wool.

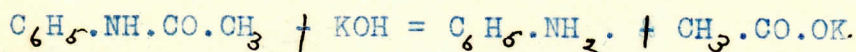
(2) Isopurpuric acid Test.- An aqueous solution of picric acid was heated with KCN solution and a solution of NaOH. Red potassium isopurpurate was formed.

(3) Ammoniacal Copper Sulphate Test.- A yellowish-green precipitate was formed.

formed upon the addition of ammoniacal copper sulphate solution to the distillate.

Acetanilide, $C_6H_5.NH.CO.CH_3$, was easily recognized by the characteristic Indophenol test which was carried out as follows: The solution was boiled with about 2 c.c. of HCl. The solution was cooled and 3 c.c. of aqueous carbolic acid solution were added. A few drops of calcium hypochlorite solution produced a violet-red color. Upon the addition of NH_4OH as a top layer, a beautiful indigo-blue color appeared.

Acetanilide is decomposed into aniline and potassium acetate upon heating with KOH.



Phenacetine, $C_6H_4.NH.OO_2H_5.CO.CH_3$, is a colorless, crystalline body which was recognized by the tests enumerated below:

(1) Chromic Acid Test.- Phenacetine was dissolved in 2 c.c. of HCl and boiled. The solution was diluted with 15 c.c. of water, cooled and filtered. The addition of a few drops of chromic acid solution produced a ruby-red color.

(2) Autenrieth-Hinsberg Test.- (a) Phenacetine dissolves to a yellow to orange-red color upon heating with dilute HNO_3 . (Distinction from Acetanilide and Antipyrine).

(b) The addition of concentrated HNO_3 gave the same result.

Antipyrine was recognized by the following tests:

(1) Tannic Acid produced an abundant white precipitate with antipyrine.

(2) Fuming Nitric Acid dissolved it to a green color.

(3) The addition of potassium nitrite and dilute sulphuric acid caused a green or blue color to appear.

Caffeine is a white, crystalline body which was detected by adding saturated chlorine water and evaporating. A yellowish-green residue remained which became purple-red upon the addition of a solution of ammonium hydroxide.

Salicylic Acid, $C_6H_4.OH.CO_2H$, is a white, crystalline body which has a sweetish, acid taste.

The following tests were made for this acid:

- (1) Upon warming an aqueous solution with Millon's reagent a deep red color was formed.
- (2) A yellowish-white precipitate was formed upon the addition of bromine water.
- (3) The addition of a solution of $FeCl_3$ caused a blue-violet color to appear.

Extraction of the Alkaline Solution with Ether.

Enough NaOH was added to the acid, aqueous solution separated from ether to make it strongly alkaline. This liberated the alkaloids from their salts. The alkaline solution was then extracted with ether. This process was repeated three or four times, and the combined ether extracts were poured into a large flask. The ether was decanted. The solution was then poured through a large filter. The filtrate was evaporated in a small glass dish upon a water-bath. Any alkaloid except Morphine, Apomorphine and Narceine may occur in the residue.

The residue was examined for:

Conine	Atropine	Codeine	Quinine
Nicotine	Cocaine	Narcotine	Caffeine
Aniline	Physostigmine	Strychnine	Antipyrine
Veratrine		Brucine	Pyramidone

These substances were tested with the general alkaloidal reagents, such as:

Mercuric Chloride	Picric Acid
Iodine-Potassium Iodide	Tannic Acid
Potassium Mercuric Iodide	Phospho-Molybdic Acid
Potassium Bismuthous Iodide	Phospho-Tungstic Acid

Purification of the Alkaloidal residue.

(1) The residue was mixed with cold water containing HCl. The solution was filtered and NaOH was added to the filtrate until it was alkaline. The alkaloids were then extracted with ether.

(2) The residue was dissolved in hot Amyl Alcohol containing a few c.c. of dilute sulphuric acid. NaOH solution was added in excess and the alkaloids were extracted with ether.

Conine is a colorless liquid which occurs in spotted hemlock (Conium Maculatum). It is precipitated by the general alkaloidal reagents.

The tests as enumerated below were made for Conine:

- (1) Solubility Test.- Conine was dissolved in enough cold water to give a clear solution. Heat was applied and the solution became milky.
- (3) Crystallization Test.- HCl was added and the solution evaporated to dryness. Needle-like or columnar needles in star-shaped clusters were formed.

Nicotine is a colorless liquid which turns yellow upon exposure to the air.

The following tests were applied for Nicotine:

- (1) Crystallization Test.- A few drops of HCl were added to the solution which was then evaporated to dryness. This yielded a yellow varnish-like substance which was amorphous. (Distinction from Conine).
- (2) Roussin's Test.- A small quantity of Nicotine was dissolved in ether. About the same volume of ether containing iodine was then added. The mixture became turbid and a brownish-red resin was deposited. After some time, ruby-red needles crystallized from the ether. These are known as Roussin's Crystals.

Aniline, $C_6H_5.NH_2$.

Some of the residue was mixed with concentrated H_2SO_4 and Potassium Dichromate solution was added. An evanescent, blue color appeared. Other tests for Aniline have been described previously.

Veratrine is a white, crystalline body prepared from sabadilla seeds (Sabadilla Officinarum).

Veratrine was detected by the following tests:

- (1) Concentrated Sulphuric Acid Test.- A few drops of H_2SO_4 were poured upon a trace of Veratrine. An intense yellow color appeared which gradually changed to orange, blood-red, and cherry-red.

(2) Concentrated Hydrochloric Acid Test.- Veratrine was dissolved in HCl. The solution was heated on a boiling water-bath and a beautiful cherry-red color appeared.

(3) Weppen's Test.- One part of Veratrine ~~was~~ ^{was} mixed with 5 parts of cane sugar in a mortar. This mixture was placed on a watch-glass and a few drops of H_2SO_4 were added. The mixture had a yellow color which later changed to grass-green and then to blue.

Strychnine, $C_{21}H_{22}N_2O_2$, which is derived from Strychnos Nux Vomica is a colorless, crystalline body which has an intensely bitter taste. Diluted with water 1 : 600,000 it can be recognized distinctly by its bitter taste.

Tests as indicated below were made for Strychnine.

(1) Sulphuric Acid-Dichromate Test.-- Strychnine was dissolved in 3 drops of H_2SO_4 on a small watch glass. A fragment of Potassium Dichromate was then added. Intense blue to blue-violet streaks shot out from the $K_2Cr_2O_7$.

(2) Physiological Test.- The ether residue was dissolved in dilute HCl. This solution was evaporated to dryness on the water-bath. The residue was dissolved in pure water. This solution was injected into the back of a small frgg. In a short time the frog became convulsive.

" Strychnine does not increase reflex irritability for all kinds of stimuli but only for tactile, optical, and especially for acoustical stimuli."

Brucine, $C_{23}H_{26}N_2O_4$, is a transparent, crystalline body. It was detected by the following tests:

(1) Nitric Acid Test.- Concentrated HNO_3 dissolved Brucine with a blood-red color which soon changed to yellowish-red and later to yellow. On the addition of a few drops of stannous chloride solution a violet color appeared.

(2) Nitric Acid - Ammonia Test.- A few drops of HNO_3 were added to brucine upon a ~~water bath~~ watch glass.

This solution was evaporated to dryness upon a water-bath. An orange-red to brownish residue remained. Upon exposure to ammonia gas the solution became grass-green.

Strychnine and Brucine may be detected when they are together by applying the Nitric Acid test for Brucine and the Potassium Dichromate test for Strychnine.

Atropine, $C_{17}H_{23}NO_3$, is a colorless, crystalline body which reacts with all of the general alkaloidal reagents.

The following tests were made for Atropine:

(1) Vitali's Test.- A small quantity was dissolved in fuming nitric acid. The solution was then evaporated to dryness. The cold solution was moistened with a few drops of a solution of KOH in absolute alcohol. A violet color appeared which soon changed to cherry-red.

(2) Odor Test.- Atropine was heated in a test-tube until a white vapor was given off. After the addition of 1 c.c. of H_2SO_4 the solution was heated until the acid began to darken. This mixture was diluted with 2 C.c. of water. During the foaming which ensued an intense, sweetish odor was given off.

(3) Physiological Test.- Atropine affects the pupil of the eye very materially. One drop of an Atropine solution diluted 1:130,000 has produced a noticeable enlargement. (This test was not performed).

Physostigmine, $C_{16}H_{21}NO_2$, also known as Eserine, is the alkaloid of the Calabar bean, the seed of *Physostigma Venenosum*.

Hot ammonia added to Eserine produced a yellowish-red solution.

After evaporation a blue-green residue remained. Alcohol dissolved this to a blue color. Excess of acetic acid changed the color to red.

Eserine produces marked contraction of the pupil. This is a characteristic action.

Cocaine, $C_{17}H_{21}NO_4$, is a colorless, crystalline substance which causes temporary anaesthesia when placed on the tongue.

Tests as enumerated below were made for Cocaine:

- (1) Concentrated HNO_3 and H_2SO_4 dissolved it without color.
- (2) Potassium Permanganate Test.- $KMnO_4$ (1:100) solution added to an aqueous cocaine solution gave a violet precipitate of Cocaine Permanganate.
- (3) Chromic Acid Test.- A few drops of 5 % chromic acid solution were added to a cocaine solution. A precipitate was formed which disappeared upon shaking. Upon the addition of concentrated HCl a crystalline precipitate of orange-yellow cocaine chromate was formed.
- (3) The material was dissolved in a few drops of dilute HCl and the solution was evaporated to dryness. The residue was dissolved in water and a small portion applied to the tongue. A peculiar, temporary, local anaesthesia was caused.

Codeine, $C_{17}H_{19}(CH_3)NO_3$, the methyl ether of morphine, is a colorless, transparent crystalline body.

The following tests were made for Codeine:

- (1) Oxidation Test.- Concentrated sulphuric acid was added to a small quantity of codeine. Potassium Arsenate was then added. Upon warming, the acid had a blue-violet color.

Furfurol Test.- Codeine was dissolved in H_2SO_4 and then warmed with a drop of cane sugar solution (1:10). This produced a purple-red color.

Narcotine, $C_{22}H_{23}NO_7$, is one of the principal alkaloids in Opium.

Narcotine was detected by the following tests:

- (1) Froehde's Test.- Froehde's Reagent (5 milligrams of Molybdic Acid dissolved in 1 c.c. of sulphuric acid) dissolved Narcotine without color.

- (2) Sulphuric-Nitric Acid Test.- A small quantity of Narcotine was

dissolved in sulphuric acid. After 1 or 2 hours a small quantity of nitric acid was added to this solution. A pronounced red color appeared.

Quinine, $C_{20}H_{24}N_2O_2$, is one of the principal alkaloids obtained from the bark of Cinchona trees. A solution in sulphuric, acetic or tartaric acid has a beautiful blue fluorescence.

The tests enumerated below were made for Quinine:

(1) Thalleioquin Test.- Quinine was dissolved in a few drops of dilute acetic acid, and 10 drops of saturated chlorine water were added. Upon the addition of ammonium hydroxide in excess an emerald-green color was formed.

(2) Herapathite Test.- A solution of 30 drops of acetic acid, 20 drops of absolute alcohol and 1 drop of dilute sulphuric acid was made. 20 drops of this solution were added to 0.01 grams of quinine. After heating to boiling, 1 drop of an alcoholic solution of iodine (1:100) was added.

When the solution had stood for some time, green leaflets with a metallic lustre were formed. This substance is an iodine compound of quinine known as "Herapathite."

Caffeine, $C_8H_{10}N_4O_2 + H_2O$. The tests for this substance have been described on page 12.

Antipyrine is an alkaloid which crystallizes in shining leaflets. The tests for Antipyrine were enumerated on page 11.

Pyramidone is a white, crystalline powder which is used in medicine as an antipyretic and an anodyne. It is a strong reducing agent, reducing gold chloride even in the cold.

The presence of Pyramidone was shown by the following tests:

(1) Ferric chloride solution added to pyramidone produced a blue-violet color which soon changed to reddish-violet.

(2) Fuming nitric acid gave to a solution of pyramidone a blue color.

(3) Bromine water imparted a grayish color to pyramidone .

EXTRACTION of the AMMONIACAL SOLUTION with ETHER and CHLOROFORM.

(a) The ether extract contained Apomorphine and traces of Morphine.

(b) The chloroform extract contained Morphine and Narceine.

Apomorphine was recognized by the beautiful, green color of the acid, aqueous solution.

The suspected solution was extracted with ether.

The solution was acidified with dilute HCl. Ammonium Hydroxide solution was added until alkaline. The appearance of the solution seemed to indicate Apomorphine, and, therefore, it was first extracted with ether.

The solution was then tested for Apomorphine, Morphine and Narceine.

Apomorphine, $C_{17}H_{17}NO_2$, was recognized by the following tests:

(1) Pellagri's Test.- Apomorphine was dissolved in dilute HCl. This solution was neutralized with acid sodium carbonate. 4 drops of an alcoholic solution of iodine were then added. An emerald-green color was formed.

(2) A. Wangerin's Test.- About 4 drops of potassium dichromate solution (0.3 per cent) were added to 1c.c. of a solution of Apomorphine hydrochloride. The solution had an intense dark-green color. This solution was shaken vigorously with 10 c.c. of acetic ether. A beautiful, violet color was formed. Upon the addition of 5 drops of stannous chloride solution (1 per cent), the color of the acetic ether layer changed to green.

Morphine, $C_{17}H_{17}NO_3$, one of the principal constituents of Opium, was detected by the modified "Staas-Otto" method. It acts as a strong reducing agent and will reduce silver nitrate and gold chloride solutions even in the cold.

Tests as enumerated below were carried out for Morphine:

- (1) On the addition of nitric acid to morphine in the solid state a blood-red ^{color} appeared which remained unchanged on the addition of a solution of stannous chloride. (Distinction from Brucine).
- (2) This test was carried out as described under Codeine. (~~Pellagri's Test~~ ^{Pellagri's Test}).
- (3) Sulphomolybdic Acid (Froehde's Reagent) dissolved Morphine with a beautiful, violet color. This color gradually passed through blue to dirty green, and finally changed to a faint red.
- (4) Formaldehyde-Sulphuric Acid Test.- This reagent ,when mixed with Morphine gave a purple-red color which successively changed to violet, blue-violet and blue.

Narceine, $C_{23}H_{27}NO_8 \cdot 3H_2O$, is an opium alkaloid having pronounced narcotic properties. It differs from Morphine and Codeine in not giving Pellagri's test.

The following tests were made for Narceine:

- (1) Concentrated H_2SO_4 dissolved it with a grayish-brown color.
- (2) Erdmann's Reagent (Sulphuric-Nitric Acid) dissolved Narceine with a yellow color which heat changed to dark orange.
- (3) Chlorine water and sodium hydroxide give a red color with Narceine.
- (4) Resorcinol-Sulphuric Acid Test.- Resorcinol-Sulphuric Acid(.01 grams of resorcinol dissolved in 10 c.c. of water) when heated with Narceine produced a carmine-red color. As the solution cooled, the color changed to a blood-red, and later to orange-yellow.

DETECTION of OPIUM by MECONIC ACID.

Meconic Acid, $C_7H_4O_7$, was detected by the following method:

A portion of the original material was extracted with alcohol containing HCl. The solution was filtered and the filtrate evaporated. The residue was dissolved in water and then the filtered solution was heated with excess of calcined magnesium oxide. This solution was filtered and acidified with HCl.

A few drops of ferric chloride solution were added. A brownish -red color appeared.

The Metallic Poisons.

A portion of the original material was put into a large flask. Enough water was added to produce a fluid mass. An equal quantity of pure hydrochloric acid was then added. Finally, 2 grams of potassium chlorate were added, the flask was shaken well, and set upon a boiling water-bath. Potassium chlorate was added in small quantities until no more chlorine was given off. The solution was filtered. The filtrate was examined for:

Arsenic	Mercury	Bismuth	Chromium
Antimony	Lead	Cadmium	Zinc
Tin	Copper		

The filtrate was saturated with arsenic-free hydrogen sulphide. The precipitate was collected upon a filter free from ash and washed with hydrogen sulphide water. The filtrate was reserved to test for Cr and Zn. The hydrogen sulphide precipitate was extracted with a hot mixture of ammonium hydroxide and ammonium sulphide solutions. The solution was filtered and tested for As, Sb, Sn and Cu. The residue was tested for Hg, Pb, Bi, Cu, Cd.

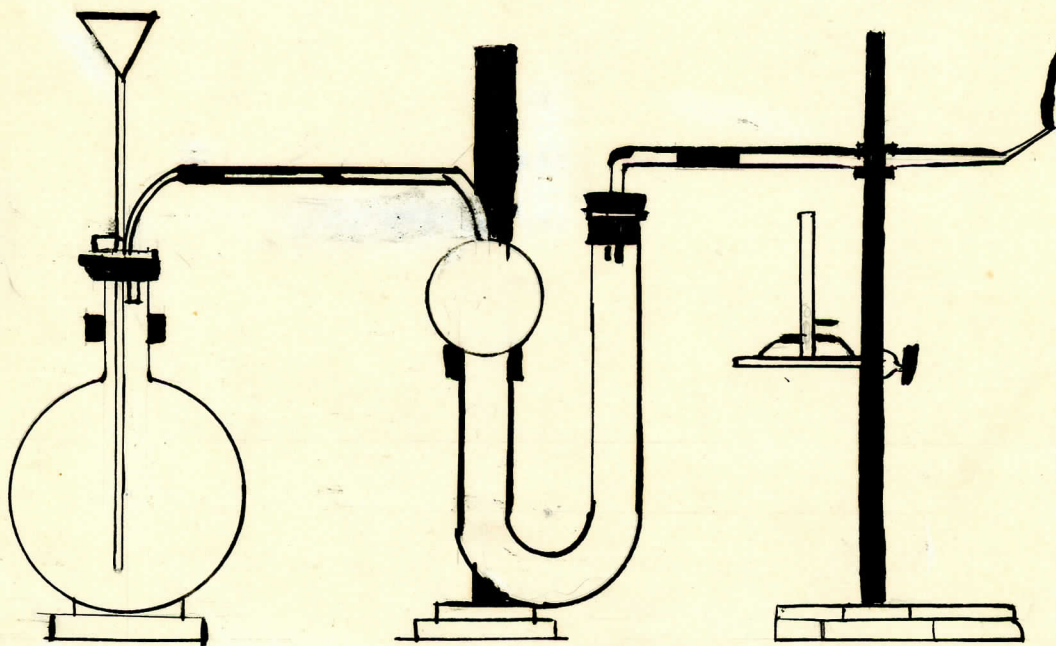
Detection of As, Sb, Sn, Cu.

The ammonium sulphide precipitate was evaporated to dryness. The residue was moistened with fuming nitric acid and evaporated again. The residue was mixed with 2 parts of sodium nitrate and 1 part of dry sodium carbonate and fused in a porcelain crucible. After cooling, the mixture was treated with hot water, acid sodium carbonate was added and the solution was filtered.

- (a) The filtrate contained As in the form of sodium arsenate.
- (b) The residue consisted of sodium pyro-antimonate, stannic and cupric oxides.

Arsenic was detected by isolating the metal in its free, elementary condition. The Berzelius-Marsh method is the best test for As and was carried out essentially as follows:

The filtrate was treated with sulphuric acid and evaporated to dryness.



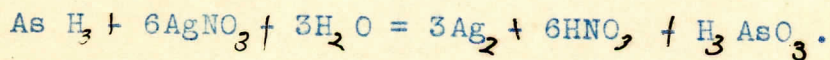
Marsh Apparatus.

Water was added to the residue and the mixture was cooled.

The celebrated Marsh's test, which rests upon the formation of arseniuretted hydrogen from the arsenic and, obtaining from the AsH_3 a deposit of metallic arsenic was then made. 30 grams of arsenic-free Zinc were placed in a hydrogen generating flask and pure, dilute sulphuric acid was added.

The gas was passed through a calcium chloride drying tube. After all the air had been expelled the gas was ignited at the exit tube. The fact that no dark spot was formed on the dish when a porcelain dish was depressed on the flame showed that the hydrogen contained no arsenical impurities. The cold, arsenical solution was introduced into the flask gradually. The nascent hydrogen combined with the arsenic forming AsH_3 .

When a piece of cold porcelain was depressed upon the flame, a rich brown-black stain of metallic arsenic was obtained. The Arsine was also recognized by its garlic-like odor. Arsine gas passed into dilute silver nitrate solution deposited black metallic silver.



Antimony was detected by Marsh's test. The method of procedure was essentially similar to that employed in the detection of Arsenic. It formed a compound of antimonuretted hydrogen (SbH_3) with nascent hydrogen.

Differences between the Arsenic and Antimony spots:

- (1) The As mirror is lustrous and metallic, brownish-black and volatile. The Sb mirror is lustreless, volatile and black.
- (2) The arsenic spot is soluble in sodium hypochlorite solution while the antimony spot is not.

Tin was detected ~~by~~ by the tests given below:

- (1) Sn precipitated white mercurous chloride (calomel) upon the addition of a solution of mercuric chloride.
- (2) The addition of a few drops of ferric chloride solution together with potassium cyanide

with potassium cyanide solution produced a precipitate of Prussian Blue.

Mercury. Tests as enumerated below were made for Hg:

- (1) A white precipitate of mercurous chloride (calomel) was formed when a solution of stannous chloride was added to the solution containing Hg.
- (2) Mercury formed a gray spot on copper.
- (3) Upon the addition of a dilute solution of potassium iodide to the Hg solution a red precipitate of HgI_2 was formed.

Tests for the detection of Cu, Bi, Cd and Pb.

Copper, Cu.

- (1) Potassium ferrocyanide solution precipitated brownish-red copper ferrocyanide.
- (2) A bright knife-blade upon being immersed in a copper solution was coated red by metallic copper.

Bismuth, Bi.

- (1) Excess of ammonium hydroxide solution was added to the solution which was then filtered. The residue was dissolved in dilute HCl. This solution was poured into a large quantity of water. A white precipitate of bismuthous oxychloride ($O=Bi-Cl$) was formed.
- (2) $SnCl_2$ and an excess of NaOH were added to the HCl solution. A black precipitate of metallic bismuth was formed.

Cadmium, Cd.

- (1) Cadmium was detected in the presence of copper by adding KCN to the blue solution until the blue color disappeared. Hydrogen Sulphide gas was passed through this solution. Yellow cadmium sulphide (CdS) was precipitated.

Lead, Pb.

- (1) After the solution containing lead had been acidified with acetic acid, potassium chromate solution was added. Yellow lead chromate was precipitated.

- (2) Potassium Iodide precipitated yellow lead iodide.
- (3) Dilute sulphuric acid precipitated white lead sulphate.

Detection of Chromium and Zinc.

Tests as enumerated below were made for Zinc:

(1) Sodium Hydroxide was added in excess to one portion of the solution. This solution was filtered and a few drops of ammonium sulphide solution were added to the clear filtrate. A white, flocculent precipitate of zinc sulphide was formed.

(2) Ammonium hydroxide solution was added in excess to another portion of the solution. After filtering the filtrate was acidified with acetic acid. Upon warming the solution, and passing H_2S through it white zinc sulphide was precipitated.

Chromium, Cr.

The following tests were made for chromium:

(1) Chrome Yellow Test.- The chromium solution was acidified with acetic acid and boiled. The addition of lead acetate solution precipitated yellow $PbCrO_4$ (Chrome Yellow).

(2) Reduction Test.- Green chrome alum was precipitated when sulphurous acid was added to the yellow chromium solution.

DETECTION of the MINERAL ACIDS.

Hydrochloric, Nitric and Sulphuric.

A portion of the original material was extracted with cold water. The following tests were made for the acids:

(1) Gunzberg's Test.- A few drops of the solution were mixed with 4 drops of Gunzberg's Reagent (1 part of Phloroglucinol in 30 parts of alcohol) This solution was evaporated to dryness. HCl and H_2SO_4 gave an intense red color. HNO_3 gave a yellowish-red residue.

(2) Sulphocyanate Test.- A solution of potassium sulphocyanate was added to a solution of ferric acetate. This solution was diluted with water until a distinct yellow color appeared. On the addition of the acid solution a blood-red color appeared.

Hydrochloric Acid, HCl, was recognized by the following tests:

(1) Chlorine Test.- Upon warming a portion of the aqueous extract with black oxide of Manganese, chlorine gas was given off.

(2) Distillation Test.- A portion of the aqueous extract was distilled. The distillate was acidified with dilute HNO_3 and silver nitrate solution was added. White AgCl was precipitated.

Nitric Acid, HNO_3 , was tested for as follows:

(1) Diphenylamine-Sulphuric Acid Test.- A few drops of a solution of diphenylamine sulphate were added to the aqueous extract. When this mixture was poured on H_2SO_4 a blue zone was formed at the point of contact.

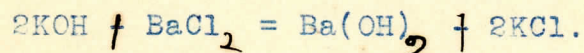
(2) Ferrous Sulphate-Sulphuric Acid Test.- The aqueous extract was saturated with ferrous sulphate solution. This mixture was poured on pure H_2SO_4 . A black zone appeared where the two liquids met.

Sulphuric Acid, H_2SO_4 , was detected by adding a solution of Barium Chloride to the solution of H_2SO_4 . A white precipitate of barium sulphate, insoluble in HCl or HNO_3 was formed.

DETECTION of the Free ALKALIES.

Potassium, Sodium and Ammonium Hydroxides.

The material was extracted several times with absolute alcohol. The combined extracts were distilled. Free Ammonia occurred in the distillate. KOH and NaOH were found in the residue. A few drops of Phenolphthalein solution and an excess of barium chloride were added to the residue. The alkaline reaction and the red color of the Phenolphthalein persisted.



(Distinction from the action of the alkaline carbonates).

Potassium Hydroxide, KOH, was detected by acidifying a portion of the aqueous, filtered extract with HCl and adding a solution of sodium cobaltic nitrite. This produced a yellow precipitate of potassium cobaltic nitrite.

Sodium Hydroxide, NaOH. The following test was made for NaOH: A portion of the filtrate was evaporated, and neutralized with HCl. Upon the addition of a solution of potassium pyro-antimonate, a white precipitate of sodium pyro-antimonate was formed.

Ammonium Hydroxide, NH_4OH . Tests as enumerated below were made for this substance:

- (1) The characteristic odor of ammonia was recognized on warming the filtrate.
- (2) The addition of Nessler's Reagent produced a yellowish-brown color.

Detection of Potassium Chlorate, KClO_3 .

Potassium Chlorate changes the red corpuscles and converts oxyhaemoglobin into methaemoglobin. The urine should always be examined in the case of suspected KClO_3 poisoning.

Parts of the cadaver were subjected to dialysis. The solution was evaporated to dryness. The residue was dissolved in water and filtered. The filtrate was examined for Chloric Acid.

(1) Indigo Test.- Dilute sulphuric acid and a solution of indigo were added to the solution until it was blue in color. Sulphurous Acid was added drop by drop until the blue color was changed to yellow.

(2) Free Chlorine Test.- Upon heating the dialysate with HCl, chlorine was set free. This gas was passed into KI solution. Shaking the solution with chloroform gave a violet color due to the liberation of the iodine.

Detection of Oxalic Acid.

Oxalic Acid, $(\text{COOH})_2$, is a powerful irritant poison and a depressant to the heart and nervous system.

Calcium oxalate was separated from the organic matter by digesting with alcohol. This solution was acidified with dilute HCl and set aside for 2 hours. The solution was then passed through a plaited filter, moistened with alcohol. Water was added to the filtrate which was evaporated to dryness on the water-bath, or until the alcohol had been expelled. The residue was diluted with 10 c.c. of water and filtered. The filtrate was extracted three times with 50 c.c. portions of ether. The total ether extract was distilled. The residue was dissolved in a few c.c. of water. Ammonium hydroxide solution was added until the solution was strongly alkaline. Saturated calcium sulphate solution was then added. The solution was acidified with acetic acid and set aside over night. White crystals of calcium oxalate were formed.

Detection of Santonin, Sulphonal and Trional.

The material was neutralized with tartaric acid and extracted with boiling absolute alcohol under a reflux condenser. The solution was filtered and evaporated to dryness upon the water-bath. The residue was dissolved in hot water. The aqueous solution was extracted 3 times with chloroform. This residue was examined for Santonin, Sulphonal and Trional.

Santonin, $C_{15}H_{18}O_3$, is a colorless, inodorous, crystalline body.

The following tests were made for Santonin:

- (1) Santonin, heated with an alcoholic solution of potassium hydroxide, gave a carmine-red color, which gradually changed to reddish-yellow.
- (2) Furfurol-Sulphuric Acid Test.- Three drops of an alcoholic solution of santonin were mixed with 2 drops of 2 per cent alcoholic furfurol solution, and then with 2 c.c. of H_2SO_4 . A purple-red color was formed which changed, upon further warming to crimson-red, blue-violet, dark blue, and finally to black.

Sulphonal, $C_7H_{16}S_2O_4$, was detected by the following tests:

- (1) Vulpius' Test.- One part of sulphonal and two parts of potassium cyanide were fused in a dry test-tube. The characteristic odor of ethyl mercaptan (C_2H_5-SH) was developed. The aqueous solution of the melt was acidified with dilute HCl. The addition of a few drops of ferric chloride solution produced a deep red color.
- (2) Reduction Test.- Upon heating sulphonal with powdered wood-charcoal, the characteristic odor of ethyl mercaptan was given off.

Trional, $C_8H_{18}S_2O_4$, was tested for by the tests enumerated under Sulphonal.