

Experimental investigation of the reactions of various copper salts with grape sugar : some new and reliable tests for sugar in urine / by George Hay, M.D.

Contributors

Hay, George, M.D.
University of Glasgow. Library

Publication/Creation

[Detroit, Mich.] : [George S. Davis?], [1885?]

Persistent URL

<https://wellcomecollection.org/works/cmpm5c4s>

Provider

University of Glasgow

License and attribution

This material has been provided by The University of Glasgow Library. The original may be consulted at The University of Glasgow Library. where the originals may be consulted. This work has been identified as being free of known restrictions under copyright law, including all related and neighbouring rights and is being made available under the Creative Commons, Public Domain Mark.

You can copy, modify, distribute and perform the work, even for commercial purposes, without asking permission.



Wellcome Collection
183 Euston Road
London NW1 2BE UK
T +44 (0)20 7611 8722
E library@wellcomecollection.org
<https://wellcomecollection.org>

Experimental Investigation of the Reactions of Various Copper Salts with Grape Sugar

—Some New and Reliable Tests for Sugar in Urine.

BY GEORGE HAY, M. D.

WITH the object in view of finding out experimentally some ready method of ascertaining beyond a doubt the presence of grape sugar in the urine, I have for many months been making experiments. When the results of these experiments are looked into it will be seen that I have adhered to one systematic method of investigation, that being, in my opinion, the only way to arrive at satisfactory conclusions. Some years ago I pointed out, in the *Phila. Medical Times*, "The Fallacy of Trommer's Test," the precise dates being July 21st, 1877, and October 27th, 1877. Since that time my opinions regarding Trommer's test have not altered in the least degree, and I am now more than ever convinced that Trommer's test is utterly unreliable as usually applied, and is, in point of fact, no test at all. When applied to a solution of grape sugar in pure water, Trommer's test will answer very well, but when applied to diabetic urine, the results are far from being satisfactory. Sugar will apparently be found when none is present, and, conversely, no sugar will be found when it is really present. The importance of knowing the presence or absence of sugar in the urine is too manifest to require any remark. I shall therefore without further introduction detail my experiments as shortly and concisely as may be done consistently with being intelligible, and I shall avoid all attempts at theorizing, although that is a much more easy thing than real experimentation. I shall detail the results in the exact order in which I made the experiments under the headings of the various copper salts.

§ 1st. CHLORIDE OF COPPER.

a. Chloride of copper, gr. j; dissolve in water f. 3 ij. in a test tube. Add solution of caustic potash in excess. Precipitates blue hydrate—protoxide of copper. Heat. Precipitate becomes black protoxide.

b. Chloride of copper, gr. j., dissolve in water f. 3 ij. Add aqueous solution of grape sugar gr. $\frac{1}{2}$, then add caustic potash in excess.—an intense blue solution. Heat. Solution becomes yellow, afterwards there forms a beautiful red precipitate of suboxide of copper. Heating continued—precipitate becomes a dirty brick red, unchanged by continued heating.

c. Chloride of copper, grs. ij., in solution: add to urine f. 3 ij. containing grape sugar gr. $\frac{1}{2}$ —greenish-grey precipitate. Add caustic potash in excess—greenish-grey precipitate becomes dissolved to intensely blue fluid. Heat. Fluid becomes first nearly black. Afterwards, fluid red by transmitted light. Upon long continued heating red color disappears and fluid contains yellowish-red precipitate of suboxide of copper. Let settle. Reduction and separation very slow.

d. Chloride of copper, grs. iv., in solution. Add to urine f. 3 iv. containing grape sugar, gr. $\frac{2}{3}$. Greenish-grey precipitate. Heat. Filter. Divide filtrate into two equal parts. To one part add caustic potash in excess—blue solution. Heat. Same changes occur as in *c.*, but much more rapidly, and precipitate separates sooner and is of a distinctly orange color. To the other portion of filtrate add a little Rochelle salt, then potash in excess—blue solution. Heat. Precipitation and reduction very much retarded by presence of Rochelle salt and the precipitate not nearly so characteristic as when the Rochelle is omitted. Takes several hours to precipitate.

§ 2nd. SULPHATE OF COPPER.

a. Sulphate of copper saturated solution, gtt. xv. Water f. 3 ij. Add potash in excess—precipitate blue hydrated oxide of copper. Heat. Precipitate becomes black protoxide.

b. Sulphate of copper saturated solution, gtt. xv. Water f. 3 ij. Solution of grape sugar, gr. $\frac{1}{2}$. Add potash in excess—blue solution.

Heat. Very soon a precipitate forms, dark orange-red, suboxide of copper.

c. Sulphate of copper saturated solution, gtt. xv. Urine, f. 3 ij., containing grape sugar, gr. $\frac{1}{2}$. Add potash in excess—blue solution. Heat. Reduction very slow. In about an hour yellow precipitate of suboxide of copper. Heating continued precipitate becomes orange-yellow suboxide. Let settle.

d. Sulphate of copper saturated solution, gtt. xxx. Urine, f. 3 iv., containing grape sugar, gr. $\frac{2}{3}$. Greenish precipitate. Heat. Cool by immersion. Filter. Divide filtrate into equal parts.

To one part add potash in excess—blue solution. Heat. Fluid becomes clear red by transmitted light, afterwards opaque, and in half an hour contains a reddish-brown precipitate of suboxide of copper.

To the other part of filtrate add Rochelle salt grs. iv., then potash in excess—blue solution. Heat. Fluid becomes clear red by transmitted light, afterwards opaque, and in ten minutes contains a distinctly yellow precipitate of suboxide of copper. It appears, therefore, that in this case precipitation is accelerated by the presence of Rochelle salt. In regard to this particular reaction I am informed that I have been anticipated as regards publication. It is a decided improvement upon Trommer's test but not half so good as some other tests of my own, which shall be detailed in this article, and which I shall particularly recommend.

§ 3d.—COPPER NITRATE.

a. Copper nitrate, strong solution, gtt. x. Water, f. 3 ij. Add potash in excess—precipitate blue hydrated protoxide of copper. Heat. Precipitate soon becomes black protoxide.

b. Copper nitrate, strong solution, gtt. x. Water, f. 3 ij., containing grape sugar gr. $\frac{1}{2}$. Add potash in excess—blue gelatinous precipitate appearing semi-solid in the tube. Heat. In a short time a dirty orange-colored precipitate of suboxide, which becomes dirtier on continued heating.

c. Copper nitrate, gtt. x. Urine, f. 3 ij., containing grape sugar gr. $\frac{1}{2}$. Greenish-grey precipitate. Add potash in excess—yields dirty blue precipitate. Heat. Reduction very slow and very imperfect, and accompanied by a great deal of white precipitate which masks the reaction.

d. Copper nitrate, gtt. xx. Urine, f. 3 iv., containing grape sugar gr. $\frac{2}{3}$. Greenish-grey precipitate very abundant. Heat. Cool

thoroughly by immersion. Filter and divide filtrate into two equal parts. To part 1 add potash in excess—an intense blue solution. Heat. In fifteen minutes yellow precipitate of suboxide of copper, which becomes orange-yellow on continued heating. Let settle.

To part 2 add Rochelle salt, grs. iv., and then potash in excess—an intense blue solution. Heat. In five minutes orange yellow precipitate of suboxide of copper. Therefore the precipitation is accelerated by the presence of Rochelle salt, and is much more characteristic. The precipitate becomes darker orange on continued heating.

The nitrate yields better results by this method than the sulphate, and it seems to me that phosphates and other interfering substances are more thoroughly removed from the urine.

§4th.—COPPER ACETATE.

a. Copper acetate, saturated solution, gtt. xx. Water, f. 3 ij. Add potash in excess—blue precipitate, hydrated protoxide of copper. Heat. The precipitate becomes black protoxide.

b. Copper acetate, saturated solution, gtt. xx. Water, f. 3 ij., containing grape sugar, gr. $\frac{1}{2}$. Add potash in excess—slight blue precipitate. Heat. Precipitate changes to yellow, and ultimately becomes a full red suboxide of copper.

c. Copper acetate saturated solution, gtt. xx or more. Urine, f. 3 ij., containing grape sugar gr. $\frac{1}{2}$. Shake the tube. Abundant grey precipitate. Add potash in excess—greater part of precipitate redissolved to a purple-blue solution. Heat. Fluid becomes clear yellow, next a dingy brown, and yields in half an hour's heating a reddish-brown precipitate of suboxide of copper.

d. Copper acetate, saturated solution, gtt. lx or more. Urine, f. 3 iv., containing grape sugar, gr. $\frac{2}{3}$. Grey precipitate persistent on shaking. Heat. Buff-colored precipitate, supernatant fluid green. Cool by immersion. Filter, and divide filtrate into two equal parts. To one part add potash in excess. Smoke colored solution. Heat. Fluid becomes yellow then brown, and in fifteen minutes deposits a reddish-brown precipitate of suboxide of copper.

To the other part add Rochelle salt, grs. iv., and then potash in excess. Yields a smoke-colored solution. Heat. Fluid goes through the same changes as when Rochelle salt is absent.

§ 5th.—COPPER OXALATE.

a. Copper oxalate, dry, fine powder, grs. ij. Diffused in water, f. 3 ij. Very slightly soluble. Add potash in excess—blue flocculent mass. Heat with shaking deposits black protoxide.

b. Copper oxalate, dry, fine powder, grs. $1\frac{1}{2}$ diffused in water f. 3 ij., containing grape sugar, gr. $\frac{1}{2}$. Add potash in excess—blue solution. Heat with shaking. Solution speedily contains a beautiful and characteristic red suboxide of copper, which upon continued heating becomes dingy red, unchanged by long heating.

c. Copper oxalate, fine powder, grs. $1\frac{1}{2}$, diffused in urine f. 3 ij., containing grape sugar, gr. $\frac{1}{2}$. Add potash in excess—white flocculi and no blue solution. Heat with shaking. Flocculi and fluid become yellow, and in twenty minutes fluid contains yellow precipitate of suboxide of copper. Unchanged by long-continued heating. This reaction is very curious.

d. Copper oxalate grs. iij., dry fine powder diffused in urine f. 3 iv, containing grape sugar gr. $\frac{2}{3}$ —greenish white mixture. Heat with shaking. Cool by immersion. Fluid contains white pulverulent precipitate. Filter. Filtrate very pale green containing very little of copper salt. Divide filtrate into two equal parts. In one part diffuse grs. $1\frac{1}{2}$ of copper oxalate. Add potash in excess—greenish blue solution. Heat. Fluid becomes yellow, then orange, and in twenty minutes heating contains reddish brown precipitate of suboxide of copper unchanged by long heating. To the other part add potash in excess—smoke tinted solution. Heat. Fluid becomes light straw color, then dark yellow orange and in half an hour heating contains a reddish brown precipitate of suboxide of copper. This precipitate unchanged by long-continued heating.

§ 6th. COPPER CITRATE.

a. Copper citrate grs. $1\frac{1}{2}$ dry powder diffused in water f. 3 ij. Sparingly soluble. Add potash in excess—blue solution. Heat. In a short time precipitate of black protoxides.

b. Copper citrate grs. $1\frac{1}{2}$ dry powder in water f. 3 ij. containing grape sugar gr. $\frac{1}{2}$. Add potash in excess—blue solution. Heat. Solution becomes yellow and soon deposits bright red precipitate of suboxide of copper. On continued heating changes to dirty brown suboxide.

c. Copper citrate grs. $1\frac{1}{2}$ dry powder in urine f. 3 ij. containing grape sugar gr. $\frac{1}{2}$. Add potash in excess—blue solution. Heat. Solution becomes yellow and in ten minutes de-

posits dirty brown precipitate of suboxide of copper.

d. Copper citrate grs. iij. in urine f. 3 iv. containing grape sugar gr. $\frac{1}{2}$. Heat with shaking for ten minutes. Cool by immersion. Grey precipitate. Filter. Divide filtrate into two equal parts. To one part add potash in excess—very pale blue solution. Heat. Fluid becomes yellow and in thirty minutes deposits a little dirty brown suboxide of copper.

To the other part of filtrate add copper citrate grs. $1\frac{1}{2}$, then potash in excess—blue solution. Heat. Fluid becomes yellow and in five minutes deposits dirty brown suboxide of copper. Very little changed by continued heating.

§ 7th. COPPER TARTRATE.

a. Copper tartrate grs. $1\frac{1}{2}$ dry powder diffused in water f. 3 ij. Add potash in excess—beautiful blue solution. Heat. Fluid remains blue for a considerable time but upon long continued heating deposits black protoxide of copper.

b. Copper tartrate dry powder grs. $1\frac{1}{2}$ diffused in water f. 3 ij containing grape sugar gr. $\frac{1}{2}$. Add potash in excess—bright blue solution. Heat. Fluid becomes yellow and in one minute deposits a characteristic bright scarlet red precipitate of suboxide of copper which changes extremely little upon long continued heating. This is the really typical suboxide of copper reduced by sugar and the more nearly we can approach to this in the examination of a urine the more satisfactory that examination will be. If there be an excess of tartrate of copper the supernatant fluid remains blue after complete settling of the suboxide.

c. Copper tartrate dry powder grs. $1\frac{1}{2}$ diffused in urine f. 3 ij containing grape sugar gr. $\frac{1}{2}$. Add potash in excess—blue solution. Heat. Fluid becomes yellow and in ten minutes deposits dirty yellow precipitate of suboxide of copper, which upon long heating becomes a very dirty yellow. Sometimes the precipitate is characteristic but no dependence can be placed on the method, although generally better than the sulphate plan *i. e.* Trommer's test.

d. Copper tartrate grs. iij diffused in urine f. 3 iv containing grape sugar gr. $\frac{2}{3}$. Heat with shaking for ten minutes. A portion of the tartrate dissolves. (There should be excess of tartrate *i. e.* a portion should remain undissolved.) Cool by immersion—buff colored precipitate. Filter. Divide the light green filtrate into two equal parts. To the

one part add potash in excess—pale blue color. Heat. Solution becomes yellow, depositing at first a whitish flocculent precipitate which becomes in thirty minutes heating a reddish brown precipitate of suboxide of copper.

To the other part of filtrate add copper tartrate grs. $1\frac{1}{2}$ then potash in excess—an intense blue solution. Heat. Solution becomes murky and in ten minutes deposits an orange yellow precipitate of suboxide of copper which is somewhat characteristic. Upon long continued heating the precipitate becomes dirty orange yellow.

§ 8th. COPPER ACETATE FOLLOWED BY
COPPER TARTRATE.

Copper acetate saturated solution gtt. xxx or more, added to urine f. 3 ij containing grape sugar gr. $\frac{1}{2}$. Shake the tube—an abundant whitish precipitate. Heat for ten minutes and then cool by immersion—precipitate very bulky. Filter, throwing the precipitate upon the filter and allowing to drain in all cases and to the filtrate add a few drops more of copper acetate to make sure that everything precipitable by it has been removed. If the fluid remains clear add copper tartrate grs. $1\frac{1}{2}$, then potash in excess—an intense blue solution. Heat. Very soon the fluid contains a bright yellow precipitate, changing to a bright orange yellow, and in very few minutes there separates a reddish-yellow or orange precipitate of suboxide of copper, which alters but little upon long-continued heating. If the tartrate is in excess the supernatant fluid is blue. This re-action is very satisfactory and the precipitate unmistakable. Let settle.

§ 9th. ZINC SULPHATE FOLLOWED BY COPPER
TARTRATE.

Zinc sulphate solution, one in ten, gtt. x, add to urine f. 3 ij containing grape sugar, gr. $\frac{1}{2}$ —an abundant flocculent white precipitate. Heat a portion of the precipitate re-dissolved. Cool by immersion and filter. Test filtrate with one or two drops of zinc sulphate solution. If it remains clear, proceed as below; if not, filter again. To filtrate, add copper tartrate grs. $1\frac{1}{2}$, then potash in excess—clear blue solution. (The potash must contain no carbonate). Heat. In one minute the solution contains a bright yellow precipitate of suboxide of copper, which, upon continued heating, becomes bright orange yellow. This reaction is quite satisfactory, and the precipitate unmistakable. Let settle.

§ 10th. ZINC ACETATE FOLLOWED BY COPPER
TARTRATE.

Zinc acetate solution, one in ten, gtt. x, add to urine f. 3 ij containing grape sugar, gr. $\frac{1}{2}$ —an abundant flocculent white precipitate. Heat—precipitate does not apparently re-dissolve to any considerable extent. Cool by immersion and filter. To filtrate add copper tartrate grs. $1\frac{1}{2}$, and then potash (free from carbonate) in excess—perfectly blue solution. Heat. In one minute solution contains bright yellow precipitate of suboxide of copper, which soon changes to a bright orange yellow, very closely resembling precipitate obtained as in § 7th b. This reaction is most satisfactory, and precipitate unmistakable. Let settle. The supernatant fluid will be blue if enough of the copper tartrate has been used. Be sure that enough of the zinc acetate has been added. It is sometimes necessary to add as much as grs. ij of the solid acetate to urine f. 3 ij before all that is precipitable by it is precipitated. If a large quantity of the acetate has been needed, the addition to the filtrate of a little Rochelle salt and dilution with half a volume of water, will much favor the reaction.

§ 11th. ALUMINA SULPHATE FOLLOWED BY
COPPER TARTRATE.

Alumina tersulphate solution, one in ten gtt. xx, add to urine f. 3 ij containing grape sugar gr. $\frac{1}{2}$. Heat—copious white flocculent precipitate. Cool by immersion and filter. Test filtrate with a little more alumina sulphate. If it remains clear, proceed as below; if not, filter again. To clear filtrate, add copper tartrate grs. $1\frac{1}{2}$, a little Rochelle salt, and then potash (free from carbonate) in excess—clear blue solution. Heat. Solution soon becomes yellow, and after one hour's heating there is a yellow precipitate of copper suboxide, which is not very satisfactory. The yellow precipitate is preceded by a white substance insoluble in excess of potash. It will be found that the less the quantity of the original precipitate, the sooner will the suboxide make its appearance. This sulphate of alumina method, though much better than Trommer's test, cannot, in my opinion, be very highly commended. Let settle.

§ 12th. ALUMINA ACETATE FOLLOWED BY
COPPER TARTRATE.

Alumina acetate, strong solution q. s., add to urine f. 3 ij, containing grape sugar gr. $\frac{1}{2}$. Heat—reddish white flocculent precipitate.

Cool by immersion. Filter. Test filtrate by addition of a little more acetate solution. If it remains clear on heating, proceed as below; if not, filter again. To filtrate add copper tartrate grs. $1\frac{1}{2}$, and a little Rochelle salt. Now add potash in excess—clear blue solution. Heat—fluid soon becomes yellow, then orange yellow, and contains a white, insoluble substance which settles first, leaving orange yellow suboxide of copper suspended above it. Let stand in tube-rack, and by and by the orange yellow suboxide will also settle, so that at the bottom of the test-tube there will be two strata of precipitate, the white, insoluble substance lowest, over-laid by the orange yellow precipitate of suboxide of copper.

This method cannot be considered so highly satisfactory as some of those already described. Still, it is reliable, and much better than Trommer's test.

§ 13th. TIN PROTOCHLORIDE FOLLOWED BY COPPER TARTRATE.

Tin chloride, strong solution gtt. x added to urine f. 3 ij containing grape sugar gr. $\frac{1}{2}$. An abundant beautiful pink precipitate. Heat. Cool by immersion and filter. Test filtrate by adding one more drop of tin solution. If fluid remains clear, proceed as below. If not, add a few more drops tin solution; heat and filter again. To filtrate add solution of soda carbonate to faint alkaline reaction and heat—yellowish white precipitate of tin oxide. Filter hot. Filtrate contains no tin. To filtrate add tartaric acid to faintly acid reaction and then copper tartrate grs. $1\frac{1}{2}$. Now add potash in excess—a beautiful, clear blue solution. Heat. In five minutes fluid becomes yellow; in ten minutes orange-yellow precipitate which almost completely separates in fifteen minutes as a beautiful orange-yellow, and thoroughly characteristic precipitate of subcarbonate of copper. Let settle—precipitate unmistakable and supernatant fluid remains blue if sufficient copper tartrate has been added. This is an excellent method.

NOTE.—The separation of the excess of tin by soda carbonate is absolutely necessary, for if this be not done the copper is not reduced to suboxide at all, but a quite black precipitate forms on heating the alkaline solution. This black precipitate consists partly of some material which is slowly soluble in hot hydrochloric acid with evolution of gas, and partly of metallic copper, which does not dissolve in hot hydrochloric acid if air be excluded, but is rapidly and completely soluble (after removal of all that is soluble in hydrochloric acid) in nitric acid or aqua regia.

oxide

§ 14th. ACETIC ACID AND LEAD ACETATE FOLLOWED BY COPPER TARTRATE.

Urine f. 3 ij containing grape sugar gr. $\frac{1}{2}$. Add strong acetic acid gtt. iij, then solution of lead acetate with shaking as long as a precipitate forms. Heat. Cool by immersion. Filter. Test filtrate by addition of one or more drops of sugar of lead solution. Filtrate remains clear, proceed as below. If not, add more sugar of lead, heat and filter again. To clear filtrate add copper tartrate grs. $1\frac{1}{2}$ and a little Rochelle salt—precipitate of lead tartrate. Never mind this. Add potash (free from carbonate) in excess sufficient to dissolve all oxide of lead at first precipitated—clear blue solution. Heat. Fluid becomes yellow and in five minutes there is a distinct orange-yellow precipitate of suboxide of copper. Let settle. Precipitate unmistakable.

Were I writing for chemists alone I should stop here and not write another word, but as the above article is intended for the use of medical men, the majority of whom are not chemists, a few additional words of explanation are necessary. When I say "Heat" I mean heat by floating the tube in water which is kept boiling as in a water bath and not by holding the tube over a naked flame. When I say "Cool" I mean that the tube is to be placed in cold water. Further, in all cases it should be ascertained that the urine contains no albumen. If it does, the albumen should be removed by heat and filtration before the above tests are applied. If the above directions are carefully followed, no matter what kind of urine is under examination, sugar will be found by the new tests which I have proposed and to which I shall refer presently under the above sections.

These investigations have cost me a great deal of labor, but—"Nihil bonum sine labore." The above tests are infinitely better than any which have been hitherto proposed, and in an experience of twenty-five years as a chemist I have tried all hitherto proposed tests for sugar in urine, Trommer's test included, and have found the majority of them worthless. I started out in the above investigations with the idea of finding but one reliable test for sugar in urine and now better than Saul, the son of Kish, I may say "Lo, I have found seven!" The seven reliable tests are described in Sections 8th, 9th, 10th, 11th, 12th, 13th, and 14th. I can confidently recommend

NOTE.—The precipitation of saccharide of lead is in great measure prevented by the acidulation of the fluid with acetic acid.

8th, 9th, 10th, 13th, and 14th, as being in my opinion excellent methods. The methods in in Sections 11th and 12th are not quite so good. Any one of these methods may easily be made a quantitative, gravimetrically, by simply washing, drying and weighing the suboxide, or volumetrically by dissolving it and adding a standard solution of some substance which will peroxidize it and indicate a final reaction.

I shall not propose any such at present. I shall only suggest that for quantitative purposes 8th, 9th, 10th, and 13th would be the best, and that of these four 8th and 13th should take precedence. For the above tests

the official "liquor potassæ" will not answer at all—it is far too weak. A suitable solution of potash may be made by dissolving six sticks of caustic potash in distilled water f. 3 ij. Twenty drops of such a solution will usually be found sufficient; if not, add more.

Throughout the above investigations there runs one general idea, viz., the separation of interfering substances, these being removed by the first precipitate mentioned in each section. As I stated at the outset of this article I shall make no attempt at theorizing but shall leave that portion of the work to be done by others.

616 PENN AVENUE, PITTSBURGH, PA.