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Observations on the assay of silver in the humid way

M. Gay Lussac

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still a gap, from the 22nd of September to the 7th of October to fill up; as soon as that is done, I will immediately proceed to a complete comparison of all observations, and think that I shall be ready with it in eight or ten days; and I then hope to be able to send you a more full and detailed communication.

Halle, Oct. 13, 1835. A. ROSENBERGER.

(*Sent as a circular by Prof. Schumacher from Altona, Oct.* 17, 1835.)

OBSERVATIONS ON THE ASSAY OF SILVER IN THE HUMID WAY. BY M. GAY LUSSAC.

There was lately sent to the Assay Office in Paris an ingot of silver, containing 3-1000dths of gold, which had been stated by one assayer to contain 990, and by another 995 thousandths of silver. Numerous assays made by M. Besseyre, to whom M. Gay Lussac had confided the process, gave 996½ thousandths of silver in the ingot; this proportion, added to the 3-1000dth of gold, gave 999½ as the sum of the precious metals. This result excited our attention, for we had never found the fine silver of commerce so pure as to exceed 997 to 998 thousandths. On the other hand, the cupellation to which the ingot was subjected to determine the quantity of gold which it contained, gave only 990 thousandths of silver, instead of 996½ found by the humid way. These results agree with those obtained by the commercial assayers, one of whom had operated in the humid way and the other by cupellation.

Surprised at so great a difference, M. Gay Lussac made researches as to its cause, and he found that it was owing to mercury contained in the ingot. On adding five milligrammes of mercury and one gramme of pure silver, he found, after dissolving the silver in nitric acid and precipitating it by common salt, that the silver had increased about four thousandths. Instructed by this synthetic experiment, he exposed 50 grammes of the ingot, in a small porcelain retort, to a very high temperature, and he obtained small globules of mercury visible to the naked eye.

The cause of the different fineness obtained by the two processes being thus known, it remained to correct it, in order to give the humid process that degree of certainty which it appeared to have lost by this unexpected circumstance; for although silver containing mercury is very rare in commerce, it is sufficient that the case has happened to put the assayer on his guard, and supply him with the means of overcoming it.

M. Gay Lussac at first thought that the mercury had not been completely oxidated, and that it would then precipitate with the silver as an insoluble chloride; but an assay of pure silver to which six thousandths of completely oxidated mercury were added in nitric acid gave 1005 thousandths, instead of 1000 as ought to have been obtained: this result proves that the mercury was precipitated with the silver.

It was then supposed that the mercury, although at the maximum of oxidation, might have been reduced to the minimum, at the moment of precipitation, by the nitrous acid produced during the solution of the silver in the nitric acid; manganate of potash was therefore added to a solution of a gramme of silver and six milligrammes of mercury, as long as it was decolorized, and even slightly in excess; but the result was not satisfactory: the quantity of the silver was increased by about five thousandths.

It therefore remained to discover the means of ascertaining the presence of mercury in silver; and this was effected by observing the manner in which chloride of silver when pure, and when adulterated with mercury, is affected by light.

It is well known that chloride of silver blackens the more readily as it is exposed to an intense light, and that even in the diffused light of a room it becomes soon sensibly coloured. If it contains four to five thousandths of mercury it does not blacken, it remains of a dead white; with three thousandths of mercury there is no marked discoloring in diffused light; with two thousandths it is slight; with one, it is much more marked, but still it is much less intense than with pure chloride. With half a thousandth of mercury the difference of colour is not remarkable, and is perceived only in a very moderate light.

But when the quantity of mercury is so small that it cannot be detected by the difference of colour in the chloride of silver, it may be rendered very evident by a very simple process of concentration. Dissolve one gramme of silver, supposed to contain $\frac{1}{4}$ of a thousandth of mercury, and only one fourth of it is to be precipitated, adding only $\frac{1}{4}$ of the common salt necessary to precipitate it entirely. In thus operating, the $\frac{1}{4}$ thousandth of mercury is concentrated in a quantity of chloride of silver four times smaller: it is as if the silver having been entirely precipitated, four times as much mercury, equal to two thousandths, had been precipitated with it.

In taking two grammes of silver and precipitating only $\frac{1}{4}$ by common salt, the precipitate would be, with respect to the chloride of silver, as if it amounted to four thousandths. In this process, which occupies only five minutes, because exact weighing is not necessary, $\frac{1}{10}$ of a thousandth of mercury may be detected in silver.

It is not useless to observe, that in making these experiments the most exact manner of introducing small quantities of mercury into a solution of silver is to weigh a small globule of mercury, and to dissolve it in nitric acid, to dilute the solution so that it may contain as many cubic centimetres as the globule weighs of centigrammes. Each cubic centimetres, taken by means of a *pipette*, will contain one milligramme of mercury.

If the ingot of silver to be assayed is found to contain a greater quantity of mercury, one thousandth for example, the humid process ought either to be given up in this case or to be compared with cupellation.

When the silver contains mercury, the solution from which the mixed chlorides are precipitated does not readily become clear.

Silver containing mercury, put into a small crucible and mixed with lamp-black, to prevent the volatilization of the silver, was heated for three quarters of an hour in a muffle, but the silver increased sensibly in weight. This process for separating the mercury therefore failed. It is to be observed that mercury is the only metal which has thus the power of disturbing the analysis by the humid way.—*Ann. de Chim. et de Phys.*, tome lviii. p. 218.

ANALYSIS OF PYROXYLIC SPIRIT.—MÉTHYLÈNE.

MM. Dumas and Peligot state that pyroxylic spirit was discovered by Mr. Philip Taylor in 1812, and that he published an account of it in 1822; and they also admit that Mr. Taylor's observations with respect to its properties are perfectly correct, and that they have procured pyroxylic spirit possessing all the properties which he assigns to it.

MM. Dumas and Peligot, in common with most chemists who have within a few years analysed any carburetted hydrogen or any substance containing carbon and hydrogen, have found a new compound of these elements, or rather, to use their own phrase, "nous donnerons le nom *méthylène* à un radical dont il est impossible d'eviter la supposition." Formerly it was deemed to be sufficiently early to name a substance when it had actually been found, but now a name is given on the *supposition* that it must exist. This radical the authors say is a carburetted hydrogen, which is the most simple of all, and is stated to consist of a volume of each of its elements, giving as its composition

4 atoms of carbon........	153·05	or	85·95
4 atoms of hydrogen......	25·00	—	14·05
1 atom méthylène	178·05		100·00

The authors then remark that méthylène, bicarburetted hydrogen, and Mr. Faraday's carburet of hydrogen are three isomeric* bodies, in which the number of the elementary atoms go on doubling, the first C H, the second $C^2 H^2$, the third $C^4 H^4$. Pyroxylic spirit yielded by analysis,

4 atoms carbon......	153·05	or	37·97
8 atoms hydrogen....	50·00	—	12·40
2 atoms oxygen......	200·00	—	49·63
	403·05		100·00

It is represented as a bihydrate of méthylène, or

1 atom méthylène....	178·05	or	44·17
2 atoms water	225·00	—	55·83
	403·05		100·00

Pyroxylic spirit when kept in a badly stopped bottle undergoes no change by contact of the air; but when its vapour and atmospheric air and spongy platina are exposed together, much heat is evolved, and formic acid is produced; while alcohol in the same circumstances produces acetic acid. During this action the pyroxylie spirit loses all its hydrogen, oxygen replacing it, so that the bihydrate

* In the commencement of the paper pyroxylic spirit is stated to be *isomorphous* with alcohol; is not this a misprint for *isomeric*?