

THE DOCTORAL THESES OF PIERRE ADOLPHE BOBIERRE (1823-1881)

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Apart from his birth on May 7, 1823, information concerning Bobierre's early life seems to be lacking (1, 2). In 1843 he was "Préparateur de Chimie" in l'École Primaire Supérieure in Paris. In the following year he filled a similar position in the Faculty of Medicine, under the direction of Jean Baptiste André Dumas (1800-1884). Bobierre obtained a diploma as "Pharmacien" in Marseilles in 1846; the route into chemistry by way of pharmacy was not uncommon at that time. By 1848 he was in Nantes and eventually died there on October 20, 1881, after a productive and varied scientific career. He appears to have attained recognition early; when he obtained his *licencié es sciences* in 1853 he had already written a number of papers as well as several books (3-5). After the appearance of the book on fertilizers (4), Dumas, who was then Minister of Agriculture, asked Bobierre to reorganize the control of these commodities. A law aimed at the suppression of their fraudulent sale was passed in 1867.

Bobierre became examiner of fertilizers in 1850. Finding that Nantes was lacking in the teaching of science, he started a course on chemistry, receiving no pay. When the Nantes School of Sciences was founded in 1855, he was appointed to the chair of chemistry and occupied this to the end of his life.

Bobierre was obviously well respected during his lifetime; he was awarded the French Cross of the Legion of Honor and received several foreign decorations (2). However, although he was active in Nantes for many years, this town, its university, and the Bibliothèque Interuniversitaire in Nancy have no record of a portrait of him.

Figure 1 shows the title page of Bobierre's doctoral theses. These were approved in the summer of 1858, when he was 35 years old (6). By then he was well established in both scientific and government circles. Dumas, the President of the examining board, was a powerful public figure and, as an internationally famous scientist, had received the Royal Society's Copley Medal in 1843. The examiners were César Mansuete Despretz (1789-1863), a celebrated physicist who was President of the Académie des Sciences in 1858, and Antoine Jerome Balard (1802-1876). Balard, most remembered for his discovery of bromine in 1826, began his professional life at the age of 17 as a laboratory boy at the Faculté des Sciences in Montpellier. From 1851 until his death, he was Professor in the Collège de France, Paris.

The longer of the two theses is devoted to "Physics" and carries the subtitle "Electrochemical phenomena which characterize the alteration, in the sea, of alloys used to sheath ships" (7). However, this thesis describes many analytical methods which have no direct connection with electrochemistry. In fact, the document is particularly valuable because it provides an excellent overview of the state of French analytical chemistry in the mid 1850's. The subtitle of the much shorter "Chemistry" thesis is "Observations relating to agriculture in the West of France" (8). A number of short accounts of agricultural chemistry are given.

Because he was the official examiner of fertilizers, it is not surprising that Bobierre should choose to deal with topics related to agriculture. However, his "Physics" thesis and related publications give no clue as to how he became involved in the completely different and

highly specialized study of metallic corrosion. Biographical (1) and obituary (2) notices do not mention this study.

Although Bobierre had published accounts of the material in his theses, these documents make almost no reference to them. In fact, referencing is minimal; often merely a name (e.g., "Davy") is all that is given. It is hoped that the references found before writing the present account are the ones that Bobierre had in mind.

Bobierre's "Physics" theme was a study of the causes of deterioration in sea water of the metallic sheathing of ships (9-12). Apparently the protection of the hulls of vessels by covering with metal plates goes back to ancient times. Copper sheathing came into use in the late 18th century. Variability of attack under sailing conditions was a problem. Commercial copper was usually impure, but the use of high-purity metal was no guarantee of long life.

Sir Humphry Davy gave much time to this problem, using as a remedy a small sacrificial anode of zinc or iron (13-15). This alleviated attack on the plates but, unfortunately, induced the formation on them of a cal-

cium-magnesium carbonate film which provided anchorage for seaweed, barnacles, and the like.

A study published in 1841 concerned the durability of the sheathing on four ships (16). All were sheathed with copper containing approximately 0.5 per cent of impurities. In two cases, this sheathing proved to be very durable; in the others, attack was severe. Yet chemical analyses of the sheathings gave no clue as to the causes of the differing performances. Factors such as differing voyaging conditions were considered. The report suggested that ships, each with the two sides carrying different kinds of copper, should be sent to sea, so that the more durable material could be selected.

Because it had been shown that some samples of impure copper performed better than the pure metal, the making of deliberate additions to copper was obvious. Thus the copper-tin alloy, bronze, came into use as a sheathing material. Bronze is harder than copper and consequently more difficult to fabricate.

Bobierre surveyed the reports of trials, made in the 1830's, on ships that were sheathed partly with copper, partly with bronze. Results varied, but the loss in weight of copper sheathing tended to be about twice that undergone by bronze. He then began the detailed examination of the bronze sheathing of various ships; one of these was the *Sarah*, the subject of a later re-examination. The sheathing of this ship, installed in 1849, became perforated and had to be replaced about a year later. Damage was not uniform; some plates were not attacked at all. He backed up his visual examination by chemical analyses, finding that the *Sarah's* sheathing contained an average of 3.1% of tin.

Bobierre surveyed existing methods before choosing his own approach. He considered the determination of tin by Sobrero's method, in which tin is volatilized in

a stream of chlorine (17). Bobierre found problems in addition to the splashing of copper chloride and resorted to classical methods, which he refined.

The weighed sample is attacked with a slight excess of nitric acid. After dilution and filtration, any lead in the filtrate is determined by precipitation as the sulfate. The residue, principally metastannic acid, is ignited and weighed. The residue, which also contains any arsenic from the alloy, is heated in a stream of hydrogen, so that the volatile arsine can be decomposed to yield a deposit of arsenic that could be compared with standards.

Bobierre drew up a table of conclusions drawn from the visual and analytical examination of the sheathings

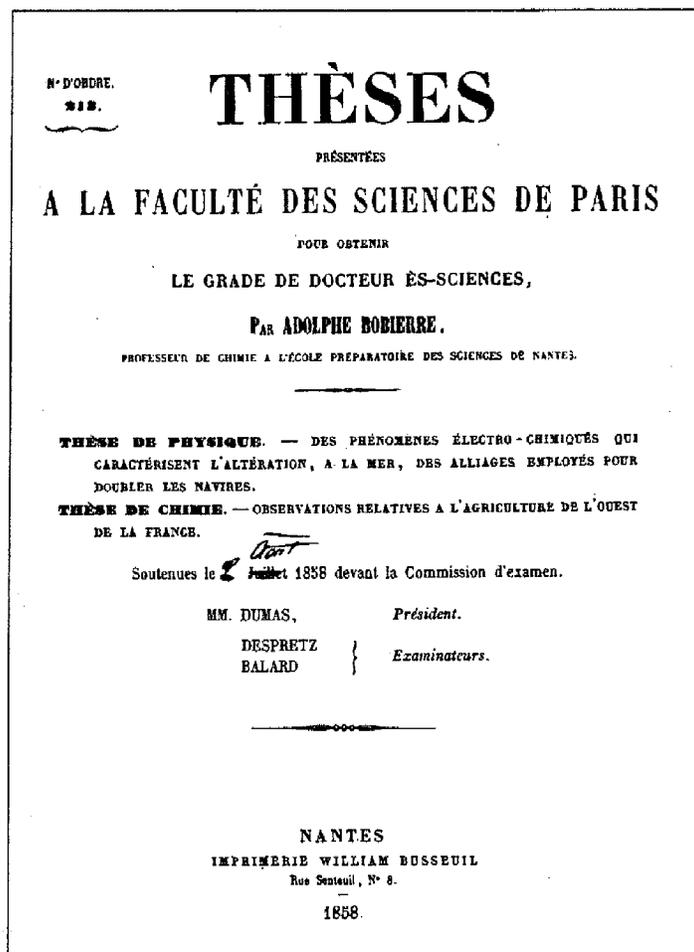


Figure 1 Title page of Bobierre's theses

used for various vessels. Although good performances had been observed with bronzes containing approximately 5% of tin, he pointed out that his conclusion was a generality. He found that attack, more noticeable at the water line, was greater near the prow of the vessel than near the stern. Obviously, sampling could not be confined to a single location.

He realized that electrochemical attack could be induced if the sheathing was not of uniform composition. He sampled bronze ingots of various copper:tin ratios, finding that the percentage of tin was greater at the surface of an ingot than in its center. The likelihood of homogeneity diminished as the average percentage of tin deviated from 5.5. Further, a bronze containing this percentage of tin proved to be very suitable for sheathing.

Bobierre had previously published his observations concerning the sheathing troubles of the ship *Sarah* (9). Obtaining a sample of the new sheathing that had been applied in 1852, he predicted that this sheathing would prove to be unsatisfactory. He deposited this prediction as a sealed letter to the Academy of Sciences (18). When the ship returned to France less than two years later, the sheathing was found to be in poor condition.

Bobierre then turned to sheathings of the copper-zinc alloy, brass, commenting that "...although relatively less durable than bronze or copper, they were in general use." (7) The performances of brass sheathings varied considerably, so Bobierre directed his attention to methods for the analysis of samples of new and of seaworn brass sheathing. Methods for the detection or determination of lead, arsenic, and iron were similar to those used for the bronze samples. Several methods for the separation of copper from zinc were surveyed. In the precipitation of copper by hydrogen sulfide or potassium sulfide, some zinc coprecipitated with copper sulfide, as had already been pointed out by Rivot and Bouquet (19). Titration, in hot ammoniacal medium, of copper with sodium sulfide solution had been described by Theophile Jules Pelouze (1807-1867) (20). However, for the analysis of brass, a difficult filtration of the easily-oxidized $5\text{CuS}\cdot\text{CuO}$ precipitate is required if zinc is to be determined (19).

Bobierre found that Flajolot's method (21) gave good results when used skillfully. He rejected this be-

cause the precipitate of cuprous sulfide, obtained by the action of "hyposulphite de soude" (sodium thiosulfate), required lengthy washing on the filter. In a method described by Louis Edmond Rivot (1820-1869) and Jean Jacques Bouquet (1827-1909), copper oxide is precipitated by the addition of potassium hydroxide. The filtrate is slightly acidified; then zinc is precipitated by means of sodium carbonate. Bobierre found that the re-

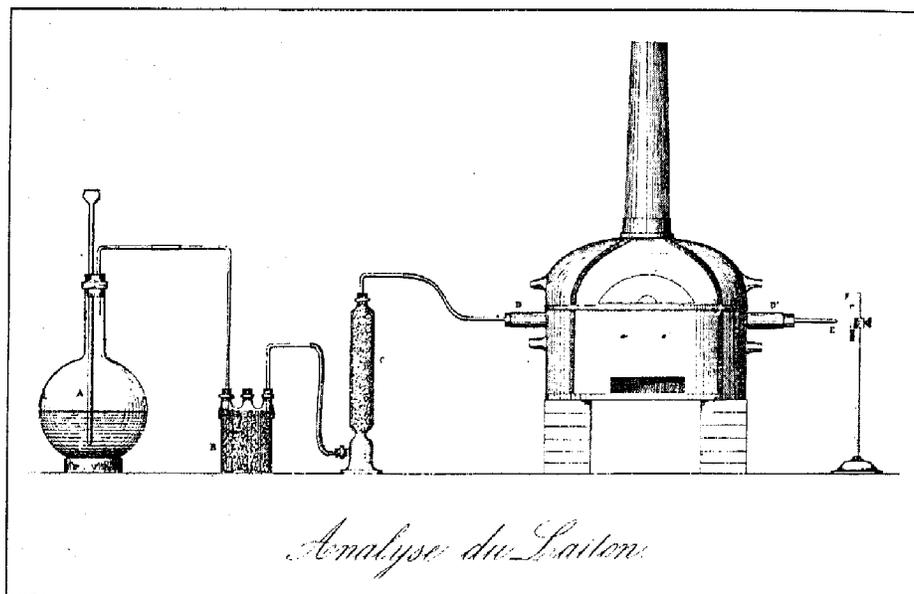


Figure 2 Apparatus for the analysis of brasses

sults for copper tended to be high.

Heating in a stream of hydrogen had been used for selective reduction in mixtures of metallic oxides (22). This principle had been adapted for the analysis of brass and bronze (23). Bobierre found that the results for zinc tended to be high. He next examined an oxidative titration method for the determination of copper (24). Copper in the solution from the sample is reduced to the cuprous state by sodium sulfite. After acidification and boiling to destroy excess sulfite, the solution is titrated with permanganate solution. He passed over this method because of variable results such as can arise from residual traces of sulfurous or nitric acids.

Bobierre next considered the loss-in-weight method used for the assay of brass coinage. Repeated furnace heatings were involved, the aim being to drive off zinc. For his purpose, the method was doubly objectionable. First, if lead is present, it is only partially volatilized. Second, the furnaces of the mint assayer were not available to the general analyst. However, the principle of selective metal volatilization appealed to Bobierre, who set about to devise a suitable method. This involved the strong heating of a weighed brass sample in a stream of hydrogen, when zinc and any lead are driven off, while

any iron or tin remains with the copper. This is obtained and weighed as a spheroidal button at the end of the operation.

The apparatus is shown in Figure 2. Hydrogen, generated in A, is demisted in B and dried by passage through calcium chloride tower C. The gas then flows through porcelain tube D, which is heated to redness. This tube contains a carbon boat into which the sample has been weighed. When the issue of white vapor from tube E appears to have stopped, disk F, which is covered with black velvet, is placed near the exit. If the velvet remains unmarked, heating is stopped and the metal button is weighed when cool. The results quoted by Bobierre indicate that the weights of the buttons thus obtained were within approximately 2-3% of the expected values.

From his 10 years of investigation of the behavior of brass sheathings, Bobierre recognized three distinct types:

1. The thickness of the sheathing diminished uniformly; neither the color nor the malleability changed much. Such behavior was usual with sheathings containing 30-34% of zinc.
2. Although there was little change in color, etc., local attack, often resulting in pitting, occurred.
3. Especially on the side exposed to the sea, the color approached that of copper and the porosity was such that finger pressure could cause fragmentation.

In other cases, otherwise satisfactory sheathing had begun to lift away from the hull, because of the corrosion of the brass retaining nails. These had contained more zinc than the sheathing and consequently suffered anodic attack. With some sheathings that originally contained 40% of zinc, the areas suffering the greatest attack had lost much of this metal. This suggested that the original material was not homogeneous and led Bobierre to survey methods used to manufacture brass sheets.

Owing to volatilization of zinc while the brass is molten, a resulting ingot may become richer in copper than expected from the proportions of the metals taken. During transport from the furnace to ingot mold, zinc tends to rise to the surface, so

the melt is stirred before pouring. However, the first portions rapidly solidify in the cool mold; but, in the slower solidification of the remainder of this pouring, various alloy phases may separate and thus lead to inhomogeneity, as Bobierre found.

Two processes were in use to convert ingots into sheets. Hot lamination, taking 24 hours and requiring only 5 heatings and 15 passes through the rolling mill, was generally adopted for brasses containing about 40% of zinc. A month was needed for cold lamination, which involved 22 reheats and coolings, as well as 66 passes through the rollers. This process was rarely used for 40% zinc brasses. In hot-laminating brass of this composition volatilization of zinc, occurring in the furnace, could be seen continuing during rolling. With brasses containing up to 20% of zinc, a black film of copper oxide formed during heating. This film could break away during rolling. Bobierre found that these effects were not observed with the apparently stable brasses containing above 20% to 33% of zinc.

Cold lamination gave a product more dense and of higher zinc content than obtainable by the hot lamination of a similar ingot. Presumably molecular stabilization and a higher density were induced by the numerous rollings needed for cold lamination. The product was found to be electronegative to one that had been hot laminated. Although they may have similar compositions, brasses from differing sources should not be used to sheath a given vessel.

Bobierre concluded that brass with the atomic ratio $2\text{Cu}:\text{Zn}$; i.e., of zinc content close to 34%, was advantageous in all respects. Insistence by sheathing contractors that the zinc content of the brass must not exceed this figure provided a guarantee against the supply of material that had been made by hot lamination, which requires an alloy with a higher percentage of zinc. Phenomena such as poor homogeneity in hot-laminated brass could cause this to deteriorate in sea water.

Bobierre's thesis on chemistry begins with a short account of the analysis of sugarbeets from various

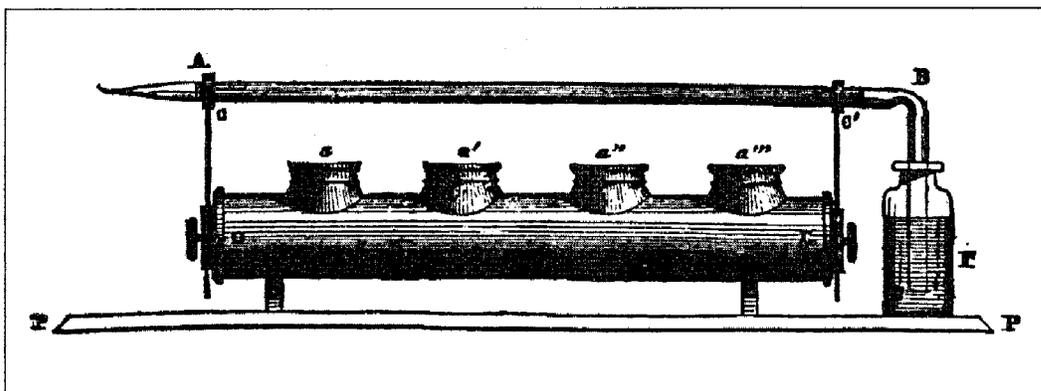


Figure 3 Apparatus for the determination of ammonia liberated from guano

sources (25). Prevailing belief was that the soils of the Loire-Inferieure region were unsuited for sugar production; he proved that this was not the case. Next follow a few pages on the flooding of the Loire and the effect on the composition of the water of this river. The great need for storage and filtration of water destined for human consumption is stressed.

Uncertainties as to quality, even adulteration, of the then important fertilizer Peruvian guano greatly concerned Bobierre. He needed a rapid method for the determination of nitrogen (i.e., available ammonia) to check such uncertainties. The apparatus (Figure 3) that he developed for this purpose was based on a principle

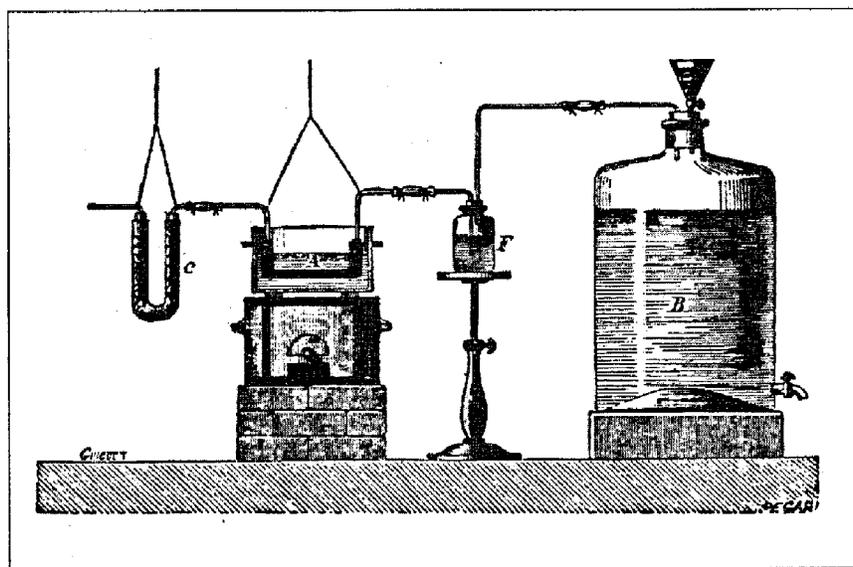


Figure 4 Apparatus for the assessment of the loss of ammonia from guano

described by Eugène Melchior Peligot (1811-1890) (26). The weighed sample is mixed with finely-powdered soda-lime and trapped between columns of the same but coarser reagent. The tube is progressively heated, starting from the end near the beak, when liberated ammonia is driven into standard sulfuric acid solution in flask F. When heating is discontinued, the beak is broken off to prevent sucking back during cooling; and the excess acid is back titrated.

Various additives had been proposed to minimize the loss of ammonia from guano that is in contact with air. Bobierre developed the apparatus shown in Figure 4 to demonstrate that "animal black" (presumably carbonized animal substances, or "animal charcoal") was effective for this purpose (27). Three grams of damp guano are placed in vessel A, which is kept at 50° C in a water bath. Outflow from aspirator B causes a fixed volume of air to be drawn through drying tube C, Vessel A, and flask F, which contains 10 cc of standard sulfu-

ric acid solution. This is back titrated at the end of the experiment. He calculated that a given sample had lost 4.3 mg of nitrogen. In a similar run in which one gram of "animal black" had been mixed with the guano, no loss of nitrogen was found.

In a further experiment, a sample of guano and another admixed with one-third of its weight of "animal black" were placed in a current of air for 10 days, being exposed to sunlight as much as possible. The mixture lost only 0.2% of nitrogen, while the loss from the additive guano was 2%.

Bobierre next reported on a rock-like fertilizer termed "guano phosphatique" (28). He then examined "animal black" in more detail, including its use in the refining of syrups (29). He found that the blackening of the copper pipes leading to the filters was caused by sulfur compounds, either present in the "animal black" or absorbed by it. Heating of the "black" with hydrochloric acid, passage of the liberated hydrogen sulfide into copper sulfate solution, and the weighing of the precipitated copper sulfide were used for quantitative studies.

After a comment on the solubility of calcium phosphate in sugar refinery residues (30), Bobierre got to the final topic of his thesis. Here was a direct agricultural problem that involved actual growing trials. It entailed a study of the release to growing vegetation of nominally insoluble phosphate. Laboratory experiments showed that slow solubilization of calcium phosphate can be brought about by a wide variety of salt solutions. The causes of the dissolution or transformation of "insoluble" phosphate in soils appeared to be very complex.

The treatment and scope of the topics in the "Chemistry" thesis are no more than might be expected of an experienced agricultural scientist. However, the study of the corrosion of the copper alloy sheathings on seagoing ships marks Bobierre as an outstanding investigator. Passing from a visual examination of the sheathings to an extended survey of methods for their analysis, he improved and developed such methods until he could be sure of his results. He then transformed himself into an industrial scientist-technologist, searching for factors beyond gross composition that might govern the performance of materials to be used for sheathing. He examined foundry practice, looking for causes of inhomogeneity during the casting of ingots. These had to be rolled into sheets, suitable for sheath-

ing; Bobierre showed that the procedure adopted had a considerable bearing on the expected performance of the resulting sheathing. Eventually, he was able to specify the composition and manufacturing procedure for sheathing which might be expected to have satisfactory durability. This work is an excellent example of the pursuit of a difficult project through all of its stages, with perseverance until a satisfactory and doubtless technically valuable conclusion had been reached.

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