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Legacy of Spanish Silver

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CHEMISTRY AS A TOOL FOR HISTORICAL RESEARCH: IDENTIFYING PATHS OF HISTORICAL MERCURY POLLUTION IN THE HISPANIC NEW WORLD

Saúl Guerrero, History Department, McGill University, Montreal, QC H3A 2T7, Canada, saul.guerrero@mail.mcgill.ca

Introduction

This article is the first of a series that explore the potential of chemistry as an efficient tool for historical research. Basic chemical principles such as the stoichiometry of chemical reactions provide the historian with a powerful tool to judge the reliability of archival records and interpret better the historiography of events that relate directly to processes of production based on chemical reactions. Chemical mass balances have determined both revenue streams and environmental consequences in the past.

A very appropriate case study to apply this approach is the first industrial scale chemical process to have caused a global economic impact. The application of mercury amalgamation to extract silver from the ores of the Hispanic New World during the Early Modern Era was a complete break in technique and scale from all previous methods used to extract silver around the world. Until the middle of the sixteenth century all refining methods applied in Europe to refine silver ores were lead-based: smelting of argentiferous lead or liquation of silver-bearing copper ores (1). In the Hispanic New World initial smelting with lead would be overshadowed by the industrial scale amalgamation of silver ores. During 250 years over 120,000 metric tons (t) of mercury would be lost to the environment through a combination of physical and chemical pathways. This article will use the chemistry of the reactions that occur during the amalgamation of

silver ores to identify and quantify the different mercury loss vectors that resulted from the amalgamation process as practiced in the Hispanic New World.

The Scale of Anthropogenic Emissions of Mercury in the New World

From 1521 to 1810 Spain produced nearly 69% of the total world output of silver from its mines in New Spain (present day Mexico) and in the Vice-Royalty of Peru (present day Peru and Bolivia). During this period there was no other non-Hispanic major silver production in the New World (2). The global economic impact of these exports of silver to Europe and China during the Early Modern Era has received wide coverage in the historiography of this period (3). The same cannot be said regarding the collateral damage to the health of the indigenous people and to the environment, suffered as a consequence of the scale of the use of mercury in the silver extraction process. To quote Richards: "the true environmental costs of silver have not been fully explored or acknowledged by scholars" (4). In the early 1530s Spain began its large scale processing of silver ore deposits mainly from New Spain and some ten years later from the area around Potosí (present day Bolivia) (5).

Smelting with lead was the refining method used in the early stages, but as of the mid 1550s in New Spain and the early 1570s in Potosí, amalgamation with mercury

was implemented, although it never managed to displace completely the use of smelting techniques. The intensive use of mercury to amalgamate silver ores in the New World led to a total loss of at least 1,253,702 *quintales* (57,670 t) of mercury in New Spain from 1558 to 1810, and of 1,386,950 *quintales* (63,800 t) in Peru from 1571 to 1810. The total losses of mercury to the environment thus amount to at least 121,470 t over a period of just over 250 years, an annual average of at least 486 t (6). This total represents the lower limit of the losses of mercury to the environment, as mercury by-products or elemental mercury, during transport, storage and amalgamation in all the mining regions of the Spanish colonies in the New World and their vicinity, without taking into account contraband or losses of mercury at the mercury mine of Huancavelica in present day Peru. It is a scale of yearly mercury losses only observed in modern times on a much wider geographical scale, though not for a continuous period of over two centuries. Anthropogenic mercury emissions registered for whole continents in the year 2000 were North America 146 t, South America 92 t and Europe and Russia 248 t. On a country level, China was the largest contributor in the year 2000 with 605 t, followed by South Africa with 257 t (7).

The environmental implications of historical mercury loss on the global depositions of mercury were reviewed initially by Nriagu, who estimated total emissions of mercury in the New World related to the production of silver at 126,000 t between 1570 and 1820, and assumed that up to 65 percent of the mercury would have been released directly to the atmosphere, with 10 percent lost during transport and 25 percent during washing or lost in the solid wastes of the process. According to Nriagu, this magnitude of airborne emissions of mercury has contributed to the present high background concentrations of mercury on a global scale (8). Camargo has also worked on the assumption that most of the silver-related mercury emissions in this period were by direct volatilization to the atmosphere at different stages of the amalgamation process. He proposes that 75 percent of his projection of 117,000 t of mercury consumed in the production of silver between 1570 and 1820 would have been lost through volatilization, the rest through losses during transport, losses in water waste and other residues. However, Camargo argues that due to the time elapsed the majority of these airborne emissions will have been sequestered mainly as marine sediments so that very little background trace remains in the atmosphere at present (9). More recently Strode, Jaeglé and Selin also assume that 60 percent of mercury used in historical mining activities was released directly into the atmosphere (10).

The most recent published research on the environmental history of silver extraction in the New World by Hagan et al. and Robins is a collaborative effort between scientists and historians, using computer modelling to establish the environment impact of projected mercury concentration levels around the historical mining sites of Potosí (silver) and Huancavelica (mercury). Hagan et al. base their projections on the assumption that 85% of mercury was lost via air emissions of elemental mercury vaporized directly into the atmosphere (11).

In order to achieve a comprehensive accounting of the different paths by which these amounts of mercury found their way to the environment it is necessary to start by reviewing the basics of the chemistry of amalgamation and combining this information with quantitative data obtained from primary historical sources. Silver ores can contain both native silver and silver compounds such as silver sulfide and silver chlorides. Mercury only forms an amalgam with elemental silver, not with the compounds. What makes amalgamation of silver ores completely different from the apparently analogous amalgamation of gold is the fact that mercury plays a double role in the former. On the one hand it is a chemical reagent that forms native silver and calomel by reducing the fraction of silver chloride present in the amalgamation mix. On the other hand it also acts to form the physical mix with the elemental silver that is called an amalgam, and as such is the fraction of mercury that is potentially recoverable from every cycle of the process. The aim of this exercise is to quantify the partition of mercury between these two roles.

Mercury Loss During Amalgamation of Silver Ores

The richest of the silver ores of the Hispanic New World were called *tacana* or *machacado*, native silver that could be worked directly with a hammer. Then came the *pacos* or *colorados*, the silver ores closest to the surface that contained silver chloride and some native silver, and finally *negrillos*, the deepest ores made up mainly of silver sulfide and silver sulfosalts (12). Wherever possible the ores with native silver were smelted with lead, not amalgamated. One of the earliest detailed accounts, from 1585, describes how the initial amalgamation process consisted in adding salt and mercury to a slurry of finely ground silver ore and water which was then heated in vats for six days. Once the amalgamation master decided the mercury had absorbed all the silver present in the ore (the step that required

the greatest skill of all) the slurry would be washed so that the lighter material could be entrained by the water and the heavier liquid amalgam stayed in the bottom of the vat. It was then squeezed through a cloth so that the excess liquid mercury was recovered at this stage. The remaining solid amalgam, called a *pella*, was then heated in closed containers to separate the silver metal from the mercury, which was recycled (13).

The first major change in the traditional amalgamation recipe was the addition of ground iron filings around 1587 as reported for Potosí, which was found to reduce the consumption of mercury. By the early 1600s the need to start refining the deeper *negrillos* which were replacing the more superficial *pacos* led to the implementation of an amalgamation recipe that now required a prior roasting of the ore and the addition of roasted copper pyrites (the *magistral*, composed mainly of copper sulfates, though roasted iron pyrites could also be used) to the traditional amalgamation mix of mercury, water and salt. In peak years major mining centres like Potosí could process nearly 700 t of silver ore in each operational day (14).

From the earliest reports it is stated that mercury was lost during the amalgamation process, even though the exact cause for the losses was initially unknown. Amalgamation lore held to the notion that one unit of weight of mercury was consumed for every unit of silver extracted. Any additional mercury consumed was due to the physical loss of mercury during operations (15). Sonneschmidt in 1804 recognizes the dual role of mercury and mentions the formation of "sweet mercury" (calomel), as a result of reactions between mercury and the muriatic acid he believed was formed during amalgamation, as well as by the reduction of the silver chloride (16). In his detailed study of Mexican silver mining published in 1843, Saint Clair Duport refers to Sonneschmidt's work and refers to the formation of a chloride of mercury both from the reduction of silver chloride and from the reaction between mercury and the copper chloride he states is formed from copper sulfate and sodium chloride during the amalgamation of silver ores (17). In his classic work on the metallurgy of silver, Percy in 1880 deals at length with experiments carried out on the conversion of silver sulfide to silver chloride in the presence of cupric chloride, water, sodium chloride and oxygen. He also comments on the reduction of silver chloride to elemental silver in the presence of sodium chloride in solution along with mercury or iron. On the subject of amalgamation he states "a large portion of the mercury used is supposed to be converted into calomel" (18).

Chemical Reactions for the Amalgamation of Silver Ores

Johnson and Whittle's work is the latest contribution based on actual laboratory experiments, and they postulate an oxidative chloride leaching since they find no major quantities of copper sulfide produced during amalgamation. The silver sulfides (the *negrillos*) are first converted into silver chloride in the presence of chloride (common salt) and Cu(II) ions (from copper *magistral*) (19):

$$Ag_2S(s) + 2\ Cu^{2+}(aq) + 8\ Cl^-(aq) \rightarrow$$

$$2\ AgCl(s) + 2\ [CuCl_3]^{2-}(aq) + S(s) \qquad [1]$$
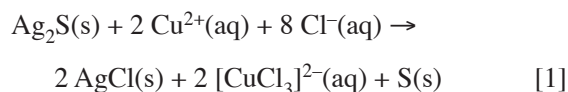
Then mercury reduces the silver chlorides either originally present or produced from the silver sulfides to elemental silver, which in turn is amalgamated by the excess mercury present in the recipe. These two steps are condensed into the following equation (19):

$$(n + 2)\ Hg(l) + 2\ AgCl(s) \rightarrow$$

$$Ag_2Hg_n(l) + Hg_2Cl_2(s) \qquad [2]$$
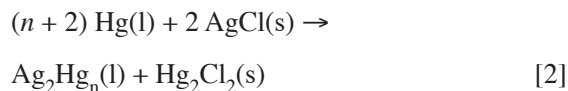
Ag_2Hg_n corresponds to the formula for the liquid amalgam. The elemental sulfur (S) that is produced can combine with mercury to produce cinnabar (Hg_2S), and any excess of *magistral* would have also consumed mercury by producing further calomel (20).

To arrive at a quantitative breakdown of how much mercury was lost through physical or chemical paths the first step is to establish a very simplified mass balance of the amalgamation of a silver ore that contains no native silver and where no physical losses are involved (Figure 1). Since it was common practice to smelt ores rich in
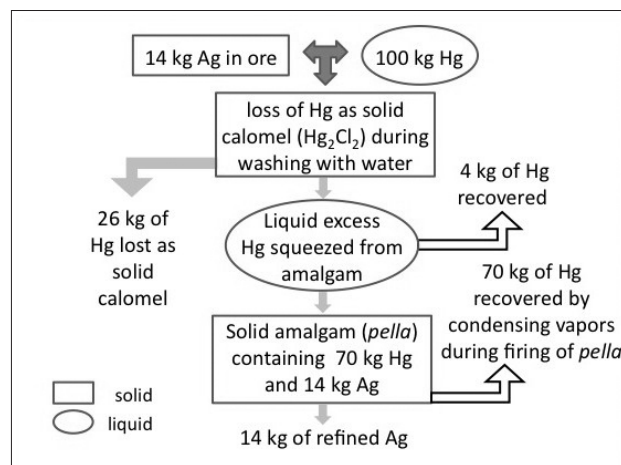

Figure 1. *Simplified mass balance of amalgamation process*

native silver rather than amalgamate them, this initial premise with respect to the nature of the silver ore is representative of the historical reality.

The total amount of mercury added to the ore during amalgamation was in proportion to the amount of silver estimated to be extracted in the ore. I will use as a starting point a proportion of seven to one in weight (21). Thus if I begin the amalgamation cycle using 100 kg of mercury, that means I am treating a quantity of ore that holds 14 kg (to the nearest kg) of silver in the form of chlorides or sulfides. It is not necessary to know the total quantity of ore treated or the exact proportion of either compound. From equation 2 it follows that every mole of silver extracted is accompanied by one mole of mercury converted into calomel. Therefore, for each kilogram of silver extracted, the amalgamation reaction consumes 1.86 kg of mercury in the form of calomel. It is irrelevant for this exercise whether the silver chloride that is reduced by mercury was present originally in the ore or is the result of the conversion of silver sulfides according to Equation 1. The assumption that matters is that no elemental silver can be produced except by the reduction of silver chloride by mercury.

I further assume that in a single cycle the totality of the 14 kg of silver is extracted, which then implies a total chemical loss of 26 kg of mercury as calomel. (Throughout this exercise I only refer to the weight of mercury lost as calomel, not to a weight of calomel produced.) In the next step of the amalgamation process the liquid amalgam containing the 14 kg of silver is squeezed and hammered very thoroughly so as to recover as much as possible of the excess mercury, leaving a solid amalgam or *pella*. The primary sources from the sixteenth century indicate that the composition of the *pella* was approximately 5 parts mercury to one part silver (22). Because of the way the model has been set up the exact composition of the *pella* does not affect the results. The *pella* now contains 14 kg of silver and 70 kg of mercury, while 4 kg of mercury were recovered by squeezing it.

In this simple model all the 70 kg of mercury will be recovered after the firing of the *pella* since for now I have assumed that there is no physical loss of mercury at any stage. In the final balance, after extracting 14 kg of silver, 74 kg of mercury is recovered in two different batches, one by a simple operation of squeezing a liquid amalgam under a twisted and beaten cloth, and the remainder by the more critical operation of heating the *pellas* and condensing the mercury vapours. In addition 26 kg of mercury are lost as solid calomel carried away in the washings.

In order to be able to correlate the results of this very simple model with historical values of the mercury to silver weight ratio it is necessary to take into account the effect of any native silver in the ore and of the physical losses of mercury. I will designate by f_a the fraction of silver present as silver chloride or silver sulfide in the ore, with values between 0 and 1. This is not equivalent to the amount of silver in an ore, only of the fraction of silver chloride and sulfide of the total silver present, whatever this may be. Thus the weight ratio of mercury lost as calomel to silver refined for ores containing native silver as well as silver chlorides and sulfides can be expressed in the following manner:

$$[Hg/Ag]_{\text{calomel loss}} = 1.86 f_a$$

If the silver content in the ore is made up of pure native silver, f_a is equal to zero and no mercury is lost as calomel. If the silver content is made up only of silver chloride and sulfide, then the weight ratio of mercury lost to silver extracted will be 1.86. I am ignoring further chemical losses in the form of secondary reactions between mercury and excess *magistral* to produce calomel or mercury with sulfur to produce cinnabar, but they could be factored into the equation in an analogous manner.

The most simple way to include the effect of physical losses on the weight ratio is to assume a single physical loss factor (f_b) between zero and unity that encompasses both mercury lost through volatilization and mercury lost through washings and spills. By taking this approach the exact amount of mercury remaining in the *pellas* does not need to be known. Based on the amalgamation recipe of seven parts mercury to one part extracted silver from the ore, the weight ratio of mercury to silver due to physical losses of mercury will then be

$$[Hg/Ag]_{\text{physical losses}} = (7 - 1.86 f_a) f_b$$

The term in parentheses on the right-hand side of the equation corresponds to the weight ratio after eliminating the chemical loss. It would be possible to separate "cold" losses of mercury (spills, washings) from "hot" losses (volatilization) but for the purpose of this exercise I will continue using a single loss factor, f_b.

The total weight ratio taking into account both chemical and physical losses can now be expressed as

$$Hg/Ag = 1.86 f_a + (7 - 1.86 f_a) f_b$$

where

Hg/Ag is the weight ratio of mercury lost to silver extracted

f_a is the fraction of silver present in the ore in the forms of chloride or sulfide, between 0 and 1

f_b is the fraction of recoverable mercury (as identified in the oversimplified model above) physically lost during amalgamation, between 0 and 1

The most appropriate cross-check for this simple model is to use the ranges reported in the historiography for the loss of mercury per weight of silver extracted, to see how well the formula can predict these historical values and how sensitive they are to both f_a and f_b.

Calomel and Historical *Correspondencia* Values

The chemical equations of the previous section tell us that in the absence of native silver in the ore and excluding other side reactions of mercury or physical losses in the amalgamation of silver ores using copper *magistral*, for every mole of silver recovered one mole of mercury would be lost as solid calomel. In this scenario, the theoretical weight ratio of mercury consumed to silver produced using amalgamation would be 1.86. How does

Table 1. Historical values of Hg/Ag weight ratios reported for amalgamation

Mercury*	Silver*	Location	Period	Hg/Ag†	Source**
1 ql	100 mk	Pachuca, New Spain	16 c	2.1	a, 165
1 ql	115 mk	Pachuca, New Spain	end 16 c	1.8	a, 184
1 lb	1 mk	New Spain	1580s	2.0	b, 175
1 ql	115 mk	New Spain	1590s	1.8	c, 175
1 ql	150 mk	Potosí, Peru	1588	1.4	d, 82
1 ql	160 mk	Potosí, Peru	1635	1.3	d, 82
13,000 lb	7800 lb	Potosí, Peru		1.7	e, 59-60
1 ql	80 mk	New Spain		2.6	c, 175
1 ql	140 mk	New Spain		1.5	c, 175
1 lb	1 mk	Honduras		2.0	f, 53
1 ql	100 mk	New World best practice	colonial era	2.1	g, 556
1 ql	85 mk	Bolaños, New Spain		2.4	g, 556
1 ql	125 mk	Guanajuato, New Spain		1.6	g, 556
1 ql	112-126 mk	Zacatecas, New Spain		1.6-1.8	g, 556
		Potosí, Peru	1750s	1.5	h, 105
1 ql	120 mk	New Spain		1.7	i, 75
1 ql	80 mk	San Luis Potosí, Sulpec, others; New Spain	1770s	2.6	i, 75
1 ql	125 mk	Guanajuato, New Spain		1.6	i, 75
1.5 mk	1 mk	Zacatecas, New Spain	1835	1.5	j, 80
12 oz	8 oz	Guanajuato, New Spain	mid 19 c	1.5	k, 118
10-24 oz	8 oz	Guanajuato, New Spain	mid 19 c	1.2-3	k, 119
1 lb	1 mk	New Spain	1836	2.0	k, 134
12 oz	8 oz	Catorce, New Spain		1.5	k, 143
15 oz	8 oz	Zacatecas, New Spain	mid 19 c	1.9	k, 251
12-14 oz	8 oz	Fresnillo, New Spain		1.5-1.8	k, 275, 279
8-13 oz	8 oz	Guadalupe, New Spain		1-1.6	k, 319, 328

*Units used: 1 mark (mk) = 8 ounces (oz) = 0.224 kg; 1 quintal (ql) = 46 kg.
†Hg/Ag weight ratio calculated from *correspondencia* values.
**Letters refer to ref. 25.

this compare with the historical data for the Hispanic New World?

Tepaske and Brown report a total of 34,184,310 kg of silver produced in Peru from 1571 to 1810, and a total of 1,386,950 *quintales* (63,799,700 kg) of mercury consumed in this period (23). This gives a weight ratio of mercury consumed to silver produced of 1.87. An analogous calculation for New Spain based on their data gives a ratio of 1.19, but since smelting may have produced up to 25% of the total silver, the adjusted ratio would be closer to 1.6 in the period 1560-1810 (24). Both are weight ratios very close to the theoretical value based on calomel of 1.86.

There is another way to test the utility of the model. Shortly after amalgamation was implemented in the Hispanic New World, the authorities applied an estimate of how much mercury was consumed by the production of silver. By controlling the consumption of mercury by each miner they hoped to avoid an underreporting of the silver extracted for the purposes of contraband. This factor was called the *correspondencia* and it is usually expressed as marks of silver per *quintal* of mercury. The theoretical weight ratio of mercury lost to silver extracted of 1.86 is equivalent to a *correspondencia* of just over 110 marks of silver per *quintal* of mercury for an ore with no native silver and with no physical losses of mercury. A selection of historical *correspondencia* values reported in the historiography is summarized in Table 1 (25). It has a greater amount of information on *correspondencia* values in New Spain but neither geographical location nor historical period are seen to play a determining role in defining the values.

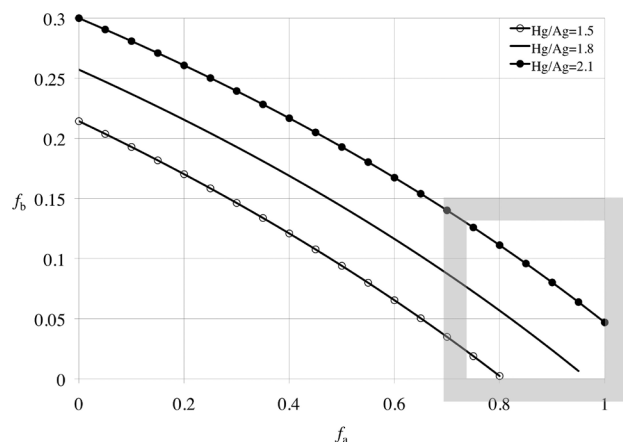The mercury to silver weight ratios have been calculated for each *correspondencia* value, and have all

been given equal weight to arrive at an average value of 1.8 ± 0.3. The *correspondencia* represented a negotiated figure that balanced the opposing interests of Crown and miners, but it is still an operational indicator of how amalgamation was implemented at each refining region. The proximity of the weight ratio based on the formation of calomel to the average historical values from both New Spain and Peru is a strong indication that the loss of mercury did not simply depend on the skill and experience of each *açoguero* (amalgamation master) but was determined to a great extent by a chemical reaction common to all amalgamation locations and historical periods.

From a purely mathematical standpoint the range of permissible physical losses of mercury is restricted both by the average values of the Hg/Ag ratio (between 1.5 and 2.1) and by the fact that amalgamation is known to have been applied preferentially to silver ores with little or no native silver content (high values of f_a, for the sake of argument > 0.75). Figure 2 illustrates the consequence of these values on the possible range of physical losses of mercury (f_b values). The lower right of Figure 2, framed in a grey box, represents both typical historical Hg/Ag values and the quality of ore one would expect would
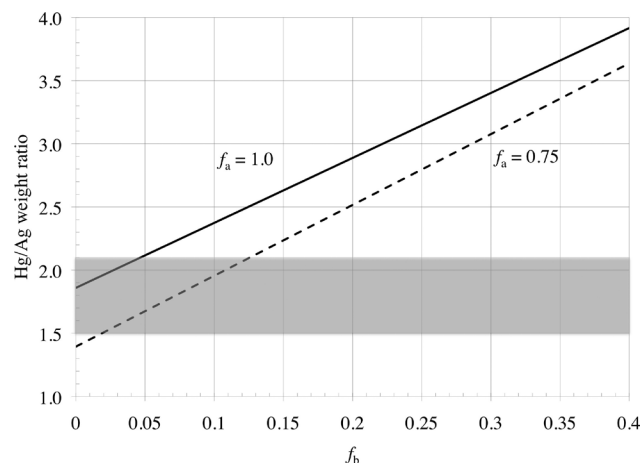
Figure 3. *Sensitivity of Hg/Ag weight ratio to f_b. (Grey band represents historically observed weight ratio of 1.5±0.3.)*

have been usually amalgamated rather than smelted during this period. The f_a values near unity represent the deeper *negrillo* ores (high in silver sulfides, very low to nonexistent native silver). In this case the average loss of mercury due to physical causes would have to lie close to the 5 to 10% range to maintain the overall mercury to silver weight ratio in the historical range. If higher physical losses are assumed to apply during the amalgamation of silver ores with low or inexistent

Figure 2. *Curves of constant Hg/Ag weight ratio as a function of f_a and f_b.*

native silver content, the mercury to silver weight ratio would quickly take on values greater than the range reported in Table 1, as can be observed in Figure 3, and such high values are not seen in the historiography. In addition, the model that leads to Figures 2 and 3 already implies minimal chemical losses, so that the inclusion of additional factors that would increase the ratio by consuming more mercury, such as the formation of additional calomel caused by excess *magistral* or the reaction of sulfur with mercury, places a further restriction on the level of physical losses. It is therefore difficult to justify persistent high physical losses of mercury during the amalgamation process of silver ores in the light of the historical range of *correspondencia* values and the nature of the silver ore being amalgamated.

Physical losses of mercury would have been one of the few variables that could be controlled by the *açoguero*, as a means to cut costs and increase profits. There is at least one contemporary voice that indicates that mercury was precisely the one parameter that an *açoguero* should control with skill, and for a very good reason (26):

> If mercury is lost [through volatilization during the firing of the *pella*] and the loss cannot be remedied ... this is the greatest loss that can be had, and it can happen to a miner during the refining process; and when it happens, not even the value of the silver [refined] can match the value of the mercury that is lost.

Duport cites mercury losses of just 0.06% during the heating of the *pella* and recycling of mercury in Mexico towards mid nineteenth century (27). Finally, at the risk of further contributing to any confusion between gold and silver amalgamation, it is significant that present day artisanal mining practices using mercury to amalgamate gold in the Amazon basin are estimated to have 5 percent vapour losses using closed containers to vaporize and recover the mercury (28). A low level of physical loss of mercury during the heating of the *pellas* may have been more the norm than the exception.

Two Exceptions: the *Beneficio del Hierro* and the *Beneficio de Cazo*

From 1587 to the early 1600s the silver refiners in Potosí applied a new variation to the traditional amalgamation recipe of mercury, salt and water. The Corzo brothers experimented with adding iron filings to the mix and found that the loss of mercury decreased (29). The reason is that iron can reduce silver chloride in saline solution (30):

$$2 \, AgCl(s) + Fe(s) \rightarrow 2 \, Ag(s) + FeCl_2(aq) \qquad [3]$$

When the Corzo brothers added iron filings to the amalgamation mix they found by accident an alternate route to reduce the silver chloride that competes with the conversion of mercury into calomel shown in Equation 2. Under these conditions the expected mercury to silver weight ratio would not be in the range of 1.9, but a much lower value determined by how much silver was amalgamated using the *beneficio del hierro*. The addition of iron filings to the traditional amalgamation recipe did not give good results with *negrillos*, which is now possible to explain since they do not have a high content of silver chloride and the silver sulfide would not be reduced by the iron. By the early 1600s the addition of copper *magistral* was found to be very effective in the amalgamation of *negrillos* and so it would soon displace the *beneficio del hierro* as the amalgamation recipe of choice. The *beneficio del hierro* would only influence the historical data in the short interval from 1590s to the 1600s (14).

The miner-priest Barba proposed in the 1610s a variation in the process using copper vats to amalgamate *pacos* using the traditional recipe of mercury, salt and water, the *Beneficio de Cazo*. Saint Clair Duport confirms Barba's initial claim that no mercury losses occur, but specifies only as long as the added mercury does not cover the whole copper surfaces of the interior of the vessel. This is not a new amalgamation recipe but a change in the batch process, which also uses greater heat to decrease substantially the amalgamation time required. It was never applied on a wide scale and gave its best results only with the richer silver ores. Whether the decrease in mercury consumption is due to the high native silver content of the ores or was the result of the interior copper metal surface of the vat having a chemical role during amalgamation is not clear (31).

Quantifying the Losses of Mercury from the Amalgamation of Silver Ores

In order to arrive at a quantitative breakdown by percentage of losses of mercury as calomel and through volatilization, one can combine the expressions used above for the calomel and physical portions of the Hg/Ag ratio. The percentage of mercury lost to calomel is

$$\%\text{Hg lost to calomel} = \frac{1.86 f_a}{1.86 f_a + (7 - 1.86 f_a) f_b} \times 100\%$$

Similarly, the percentage lost to physical processes is

$$\%\text{Hg physical loss} = \frac{(7 - 1.86 f_a) f_b}{1.86 f_a + (7 - 1.86 f_a) f_b} \times 100\%$$

Bear in mind that these physical losses include losses by volatilization, so they can be interpreted as an upper limit to emissions of mercury to the atmosphere.

Table 2 provides a summary that indicates a loss of mercury as solid calomel that accounts for 66 to 93 percent of total mercury losses, while physical losses would have been in the range of only 7 to 34 percent. The parameters of two of the entries in Table 2 are taken from the left edge of the "frame" in Figure 2; they represent the upper and lower limits of typical Hg/Ag weight ratios and an ore that has a relatively large amount of native silver. The additional point corresponds to an ore containing no native silver and a Hg/Ag weight ratio at the high end of the average historical range.

Table 2. Percentage breakdown of mercury losses to the environment as a result of the refining of silver ores with mercury

f_a	0.75	0.75	1.00
f_b	0.13	0.02	0.05
Hg/Ag	2.1	1.5	2.1
% mercury chemical loss as calomel	66%	93%	88%
% mercury physical loss	34%	7%	12%

Instead of the majority of the mercury emissions (from 60 to 75 percent) taking place as direct volatilization of elemental mercury, up to nine tenths of the mercury pollution would have been in the form of solid calomel washed downstream or buried in landfills from each refining unit (*ingenio* in Peru, *hacienda* in New Spain). Losses during transit or storage plus additional consumption of mercury due to side reactions with *magistral* and sulfur would need to be factored in, but they do not alter the fundamental change in how the historical impact of mercury losses should be analyzed.

Conclusions

Spanish miners in the Hispanic New World were the first in history to apply amalgamation with mercury to silver ores on an industrial scale. From the start they realized that they were losing mercury no matter how skilled they were in distilling the mercury and recovering it by cooling the vapours with water in a special vessel. They had workers recovering the fine silt, or *lamas*, and

heating them to extract whatever silver and mercury may have been entrained in the washings. Even the coarser sediment, the *relaves*, could be sold to those looking to recover the last ounce of mercury and silver from each cycle of amalgamation. In spite of these efforts to maximize the recycling of mercury, within the first thirty years a rule of thumb was established that approximately two weights of mercury would be lost for each weight of silver recovered.

Up to now this weight ratio or *correspondencia* has been commented upon in the historiography as an empirical number with no theoretical justification (32). However the application of the principles of stoichiometry to chemical reactions that are known to occur during amalgamation provides a chemical underpinning to the *correspondencia* that has not been clearly defined before. This theoretical base converts the *correspondencia* from a passive mirror of operational empiricism into an active tool of historical analysis. Using the same simple model that can explain the historical ranges observed for the *correspondencia*, it can also quantitatively break down the vectors of mercury loss into calomel and physical losses. The result is a completely different scenario from that assumed in most studies published to the present. Calomel is the form in which up to 90% of mercury is lost from refining centres using amalgamation, not volatized mercury (33). The impact of historical mercury loss from silver refining centres therefore needs to be re-examined on the basis that most of this mercury would have been washed away or buried as solid calomel, together with the even larger amount of detritus from the amalgamation operation. The combined risk that calomel and elemental mercury posed to people and the environment during two and a half centuries of continuous silver amalgamation in the Hispanic New World is currently under study. In principle if the amount of mercury consumed or silver refined by amalgamation is available in the official data, it is possible to estimate the quantities of calomel and elemental mercury that would have been issued to the environment. As the next paper will show, the problem lies in determining which, if any, of the historical archival data sets on mercury and silver is reliable enough to arrive at a true value of the extent of mercury losses to the environment.

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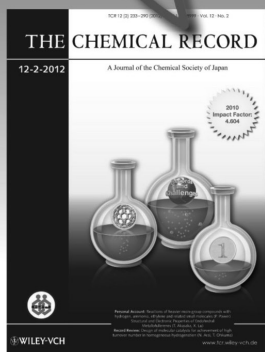
About the Author

Saúl Guerrero received his degree in Chemistry at the Universidad Simon Bolivar (Venezuela) in 1975 and a Ph.D. in Polymer Physics from Bristol University (UK) in 1980. After a career of teaching and research in the area of polymers and then as an international marketing manager for a major oil company, he obtained an M.A. in Global History at the University of Warwick (UK) in 2009 and is at present a Ph.D. candidate in the History Department of McGill University thanks to the award of a Peter Cundill Fellowship.

CHEMISTRY AS A TOOL FOR HISTORICAL RESEARCH: ESTIMATING THE CONTRABAND OF SILVER FROM POTOSÍ AND ORURO, 1576-1650

Saúl Guerrero, History Department, McGill University, Montreal, QC H3A 2T7, Canada, saul.guerrero@mail.mcgill.ca

Introduction

Historical contraband is a topic that is very difficult to quantify since by its nature it is hidden from production or sales data available in archival records. It is not only a question of the commodity that is the being trafficked as contraband. Even the data on the raw materials required to produce it may be open to question if those materials could also be obtained outside the official channels of distribution. This can leave the historian without a reliable point of reference on which to base calculations. Silver production in the Hispanic New World is a very appropriate case in point. All the historical official silver and mercury production data from the Spanish colonies in the New World are assumed to be an incomplete picture of production levels and practices, due to a combination of contraband and a bureaucracy that was lax, corrupt or both (1). It has been estimated that as much mercury was sold as contraband as was consumed in the Vice-Royalty of Peru (2). In the case of silver the educated guesses of historians have placed the level of contraband anywhere from very low up to twice the official production levels (3). Both sets of official data are thus expected to report values below the real levels of production, reflecting the evasion of tax payments to the Spanish Crown on the true amount of mercury and silver produced in any given year. Contraband of mercury would in fact have a double negative impact on the tax receipts, once on the mercury itself and then on the silver that could have been officially produced from it. This is the reason why con-

traband mercury was more expensive than the mercury made available through official channels (4).

The workers at the mercury mine of Huancavelica (modern day Peru) are said to have been driven to selling contraband mercury because the Crown was always in arrears in paying for the mercury that was purchased under the Crown monopoly (5). In the case of silver the search for greater profit would have been the only motivation. There were at least four ways to circumvent the payment of royalties on any silver produced (6):

1. By officially declaring less silver than was obtained via amalgamation with mercury supplied by the Crown. This would be best accomplished by negotiating the *correspondencia* value with the local authorities.

2. By underreporting the official silver production with the connivance of the local Crown officials.

3. From the smelting of the richest silver ores using lead, thus avoiding having to purchase official mercury supplies.

4. From amalgamation of silver ores using contraband mercury.

To detect any of these paths is not straightforward. To avoid the first option the Crown established by the end of the sixteenth century that there was a rule of thumb correlation between the average amount of

mercury that was lost during amalgamation and the weight of silver extracted. This correlation was called the *correspondencia*, with a range of values that on average corresponded to a weight ratio of mercury consumed to silver extracted of 1.8 ± 0.3 (7). In some jurisdictions fresh mercury would only be supplied to the refiners on the basis of the mercury declared to the Crown as having produced the registered amount of silver (the *consumido*) (8). One way around this control would have been to negotiate with the Crown authorities a higher mercury to silver weight ratio (corresponding to a lower *correspondencia* factor) than actually required by the refiners, which would have supplied them with excess mercury. Indirect evidence for this would be increases in the recorded weight ratio compared to previous average levels.

The last three methods of obtaining contraband silver do not leave any trace in the production records other than the suspicion left by decreases in production that cannot be readily explained through other causes. If the contraband in question is not the household industry variety but is suspected of reaching major levels of output then all four contraband options require an existing plant infrastructure capable of physically processing sufficient silver ore to supply both the official production of silver and the silver to be trafficked as contraband. The silver ore had to be ground in large stamp-mills to the correct mesh size and afterwards treated with mercury and additives in many vats (9). This is the Achilles' heel of any contraband operation based on industrial infrastructure: books can be doctored with care and officials bribed, but stamp mills and amalgamation vats cannot be hidden.

Once capital-intensive production units are built, it is in the interest of the investor to maximize his return on the capital invested by producing at the limit of what his plant would allow. There are historical circumstances that may have imposed an idling of installed silver refining capacity, such as problems with the work force, interruptions of supply of needed raw materials, epidemics, lack of sufficient rainfall to drive the water-mills, changes in ore quality, and others. However, if on a long-term basis a production unit built with private capital is observed to apparently run well below its nominal capacity without defaulting on its financial obligations, and it happens to be producing a commodity that has a high contraband value and market demand, then the difference between registered output and nominal capacity can provide an independent guide to the potential order of magnitude for contraband.

Production of Silver in the Vice-Royalty of Peru, 1576-1650

In the first 75 years after the definite introduction of amalgamation of silver ores in the Vice-Royalty of Peru (1572-1574), 93% of all the silver officially accounted for was produced just from the mines and refining centers (*Ingenios*) of Potosí and Oruro (Figure 1) (10). Amalgamation would have been firmly established as the main refining process by 1576 (11). The turn of the century was a watershed in the history of amalgamation in the Vice-royalty of Peru. The period from the mid 1570s to 1585 had seen production of silver rise by nearly nine times after the introduction of the initial amalgamation recipe (Figure 2) (7). A decrease in production after 1585 drove the refiners to search for an improved amalgamation recipe. By 1588 the Viceroy was worried that attempts to find a more efficient use of mercury would endanger the revenues and taxes from the Crown sales of mercury if refiners managed to decrease its consumption. He therefore commissioned a technical audit of all the trials that were being carried out in Potosí to improve the traditional amalgamation recipe, and prohibited any more trials being carried out without official authorization (12). The audit reports that in 1587 the Corzo brothers had obtained positive results by adding finely ground iron metal to the amalgamation mix, the *beneficio del hierro* (13). It also includes among its list of trials the addition of a blue mineral (*copaquiri*, copper sulfate) to the amalgamation recipe (14). However it would only be in the early 1600s that the amalgamation process would incorporate as standard procedure a prior roasting of the ore and the addition of copper *magistral* (copper sulfate from roasted copper pyrites) to the traditional recipe of water, salt and mercury. This was the most efficient amalgamation process that allowed refiners to extract silver from the *negrillos* (silver sulfides) that had displaced the *pacos* (silver chlorides and native silver) as the main type of ore coming out of the mines of Potosí (15). Finally in the late 1610s Barba would propose his new way of refining *pacos* by cooking (*cocimiento*) the amalgamation mix in copper vessels, the *beneficio de cazo* (16). No other period in the history of Potosí would be witness to so many successful innovations applied to the amalgamation process.

By 1650 other mining centers in Peru would contribute larger shares of the total production of the Vice-Royalty. To avoid having to make assumptions on how mercury was distributed to each mining center I have chosen 1650 as the cut-off date for my analysis. For the pur-

poses of the exercise all the mercury registered as produced at Huancavelica or imported into Peru from Europe during these years is considered consumed at Potosí and Oruro. No correction will be made for any supplies to New Spain from Huancavelica during this period (17). Since there is a delay between production of

Figure 1. *The Vice-Royalty of Peru in the sixteenth and seventeenth centuries*.

mercury and consumption at the Ingenio this introduces a distortion in short term correlations of data. Bakewell when faced with a similar problem staggered the data sets he compared by one year (18). Since the effects of back-ups of mercury within the whole official distribution system are not necessarily dissipated within one year, as shall be seen for the case of the decade 1601 to 1610, I prefer to simply acknowledge this degree of uncertainty in the method I employ.

In the case of the official data on silver production, the primary sources used by historians are not actual production outputs measured in units of weight, but the amount of tax collected at each of the regional Treasuries (*Caja Real*). Refiners brought the refined silver to the *Caja Real* of Potosí or Oruro, where officials would calculate the tax to be paid. Over a fifth of the silver was retained in order to pay for the royal taxes, the *quinto* or fifth plus an additional tax, the *derecho de Cobos*. The amount of silver that must have been produced is calculated based on the tax records (19). On the other hand, according to Whitaker, sales of official mercury were used to
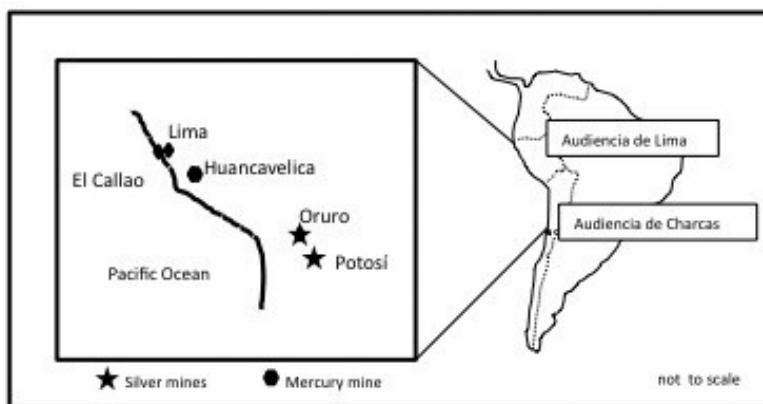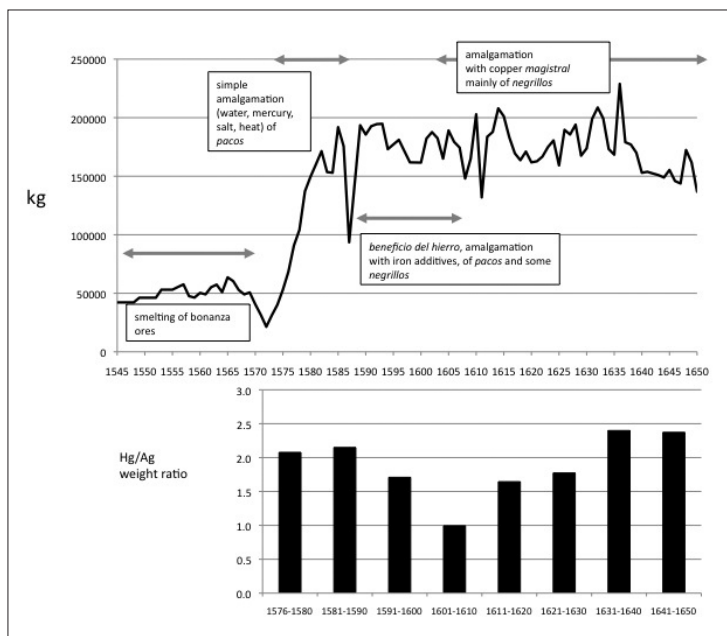
estimate the amount of tax on the deemed silver produced via amalgamation: "[the Crown] protected itself against tax evasion on the part of the latter [silver miners] by computing the *quinto* ... not on the basis of the silver which the miners reported they had produced, but on the basis of the amount of mercury which the records of the mercury administration showed they had bought" (20). Though Whitaker does not mention how the officials arrived at the deemed production level of silver it must have been on the basis of the *correspondencia* factor. This calculation of an estimated production using the *correspondencia* factor avoided the problem of silver refiners bringing less silver to the *Caja Real* than they had refined, and then requesting again the same amount of mercury as the last batch. It is possible that both methods were applied concurrently or that practices differed according to each locality.

The other caveat regarding the official data on silver production in Potosí is that in at least one period it is shown to be completely divorced from events on the ground. In 1626 one of the dams built to create water reservoirs above the city gave way with devastating consequences. When the dam broke the resulting flood is reported as having destroyed 126 out of 132 *Ingenios*, 76 of which were claimed to be beyond repair (21). In spite of this, silver production (in marks) derived from the tax records shows an increase from 570,171 in 1626 to 594,682 in

Sources: Silver production from Ref. 10, 188-191; mercury to silver weight ratios from Table 1.

Figure 2. *Annual production of silver (official) from Potosí and Oruro and mercury to silver weight ratio*.

1627, reaching a peak of 646,543 in 1628, and then dropping to 536,473 in 1629 (22). Even taking into account possible delays in the register of production data the loss of over half the *Ingenios* should have been reflected in the official production data, unless the extent of the damage was misrepresented in the primary sources.

In spite of all these elements of uncertainty and change, the calculation of the mercury to silver weight ratio using the official figures of mercury and silver production for Potosí and Oruro provides a remarkably consistent picture for the period in question. The average value of this ratio in Table 1 for the period 1576 to 1650 is 1.9 ± 0.37. The use of the mercury to silver weight ratio as an analytical tool for the study of the historical production of silver is not new (see below) but what is novel is the proposition that it is a factor determined by the stoichiometry of the chemical reduction of silver chlorides by mercury, and not an empirical number. The range of values of this ratio in Table 1 correspond, with one sole exception, to what is expected from an amalgamation reaction based on the reduction of silver chlorides with mercury (7). The conclusion is valid whether the production data of silver and mercury are derived from actual physical quantities or if the official silver production was calculated from the official mercury supplied to the refiners.

Table 1. Mercury and silver official production data, in metric tons, 1576-1650

period	silver[a]			mercury[b]	weight ratio Hg/Ag
	Potosi	Oruro	Potosi + Oruro		
1576-1580	550	0	550	1143	2.1
1581-1590	1622	0	1622	3486	2.1
1591-1600	1770	0	1770	3025	1.7
1601-1610	1708	68	1776	1766	1.0
1611-1620	1373	389	1762	2898	1.6
1621-1630	1308	447	1755	3111	1.8
1631-1640	1340	517	1857	4453	2.4
1641-1650	1152	370	1522	3611	2.4

Sources:

a) Ref. 10, Tables 4.5 and 4.7, 188, 191.

b) Ref. 2, 264 and Appendix V, 453-54; Ref. 17, Tables 1 to 4, 1959-1965.

The only exception to the above is the decrease of the weight ratio to unity in the decade from 1601 to 1610. This reflects the increasing impact of the implementation

of the *beneficio del hierro* from the late 1580s to the early 1600s before it was phased out by amalgamation using copper *magistral* (23). The iron in the *beneficio del hierro* competes with mercury for the reduction of silver chloride to form elemental silver and calomel, so that consumption of mercury would decrease for the same amount of silver refined. This is the explanation to the observation by a refiner in the sixteenth century that "with the new iron process ... even though not much silver was extracted, no mercury was lost" (24). That the *beneficio del hierro* played a major role in the amalgamation of silver ores in Potosí up to the early 1600s is indicated by the 1603 report that 4,000 *quintales* (184 tons) of iron were used to refine silver that year, though no breakdown exists to quantify its overall share of the refining process (25).

The impact on mercury demand would be felt from the 1590s to the early 1600s, tracking the rise and fall of the *beneficio del hierro*. Lohmann Villena has documented the accumulation of 17,000 *quintales* (782 tons) of unused mercury by 1604 in the inventory of Huancavelica. The Crown had committed to purchase amounts of mercury based on historical levels (pre-1587) when no *beneficio del hierro* existed. Lohmann Villena also argues that the Crown preferred to purchase as much as possible from the Huancavelica miners so as to avoid contraband sales of mercury. Faced with a glut of mercury the Spanish authorities imposed strict limits of production in 1604 (only 859 *quintales* were produced in that year, down from previous levels over 5,000 *quintales*) and the decrease in production levels lasted until the end of the decade (26). The system had backed up because now less mercury was consumed for equivalent amounts of silver production. It would seem that the Viceroy Don Fernando de Torres y Portugal had been correct in fearing a sharp decrease in the Crown sales of mercury due to new improvements in the amalgamation recipe. The ability of copper *magistral* to efficiently convert the silver sulfides of the *negrillos* into silver chlorides would eliminate the use of the *beneficio del hierro*.

Does the profile of the mercury to silver weight ratio throughout this period provide any guide as to the presence or extent of contraband, once the effect of the change in amalgamation recipe has been accounted for? The ratio stays within the average historical range of 1.8 ± 0.3 except from 1631 to 1650 when it reaches 2.4, indicating that much more mercury was being used than previously. This would imply either a lower efficiency in the physical recycling of mercury or that mercury was also being used to produce contraband silver.

Can the weight ratios in Table 1 provide any indications as to the contraband of silver obtained by smelting after the introduction of amalgamation? By themselves the ratios can only indicate if enough silver produced by smelting was declared to the Crown so as to decrease the weight ratio beyond the average deviation observed in the historical *correspondencia* values. Thus the value of unity explained by the *Beneficio del Hierro* could also be explained by a surge in smelting of official silver that would account for a significant decrease in the use of mercury. As to contraband silver, it would only be inferred if independent evidence showed that smelting produced large quantities of silver in any given period but the mercury to silver weight ratio did not decrease significantly below 1.5.

One independent source to estimate an order of magnitude of total silver produced by smelting is a study carried out by Abbott and Wolfe of lead deposits in core samples taken from the sediments of a lake in the vicinity of Potosí. The concentration of lead per gram of sediment is correlated to different periods in time, from the year 600 to the present. The plot shows a prominent peak with a concentration of just under 300 μg/g around 1550, the period when Spanish miners were producing silver using only smelting. After amalgamation was introduced the concentration of lead begins to decrease, but it is quite an asymmetrical peak, since between ca. 1600 and 1650 a shoulder persists around a concentration level of approximately 225 μg/g (27). The authors of the study recognize that the high overall levels of lead deposits in the lake are the result of lead smelting to refine silver. The concentration of lead can be taken to be directly proportional to the amount of silver that was being extracted by smelting in the period 1550s to 1650, if the loss of volatilized lead per unit of silver refined by smelting remained relatively constant. In the period 1550 to 1572 an average of at least 50 tons per year were produced by smelting of silver ores with lead (28). A rough estimate would place the level of smelting from about 1600 to about 1650 at around 35 tons of silver by smelting, proportional to the average 25% decrease observed in the concentration of lead in the lake sediments, all other factors remaining equal. This level of smelting is too low to decrease substantially the Hg/Ag weight ratio beyond its expected average historical range, so it cannot be assigned unambiguously as having been destined either for contraband or registered as official production. However it can be ruled out as having been the major factor responsible for the decrease in weight ratio to unity in the decade 1601-1610.

Infrastructure Limitations on Silver Refining in the *Ingenios*

The bottleneck to the production of silver by amalgamation, whether official or contraband, was the maximum rate at which the mineral could be processed through the stamp-mills and the amalgamation vats in the context of an industrial batch process. In the discussion that follows I will limit my attention to Potosí towards the end of the sixteenth century because of the availability of infrastructure data for that time and place. In 1585 Luis Capoche, a Spaniard who owned *Ingenios* in Potosí, published a list of the *Ingenios* existing at the time, with their location, the number of heads and stamps used for crushing the ore, and their source of power (water or horse). Thanks to the data published by Bakewell on the processing capacity of these types of mills it is therefore possible to arrive at an estimate of the physical limit to the amount of ore that could be ground in these *Ingenios* in an average year during this period (29). Table 2 provides a summary of the calculated milling capacity for Potosí around 1585, and an annual total estimated at 3.4 million *quintales* based on a 200 day operating period in a year (30). Capoche mentions a much lower annual capacity of 1 million *quintales* of ore, of which according to his estimate only 600,000 *quintales* were actually processed. If his estimate was correct it would require the silver content of the ore to be around 10 pesos per *quintal* to produce the official quantity of silver reported on average for the decade of the 1580s. This is contrary to the information given throughout Capoche's work on the silver content of the ores in this period (31).

A separate document with detailed information on Potosi, dated 1603, coincides with the estimates given in Table 2. The anonymous report states that 2.7 million *quintales* of ore were brought down from the mountain to be processed in one year. It also provides the information that there were 128 stamp heads in operation, each capable of processing 150 *quintales* of ore per day, so that in 200 days (the assumption used in Table 2) a total of 3.8 million *quintales* would have been processed. Finally, according to the same primary source 4,262 *quintales* of silver were refined from the 2.7 million *quintales* of ore, which indicates a silver content in the ore of 2.7 pesos per *quintal* (0.16% by weight of silver) (32). The information in this document is more consistent with what is expected of the silver content of these ores from the majority of Capoche's work. Since the output calculated in Table 2 is based on a separate 1576 document used by Bakewell to calculate the ore processing capacity of the stamps, the data from 1603 provides strong independent support

Table 2. Estimated installed milling capacity in Potosí, 1585.

Ingenios	Type	total stamps	*quintales* ore per day per stamp	total *quintales* ore per day	sub-total *quintales* ore for 200 days	total *quintales* of milled ore for 200 days
75	Water	823	19.75	16,250	3,251,000	
31	Horse	231	3.02	698	140,000	
						3,390,000

Sources: Ref. 19 (Capoche), 118-122; Ref. 11.

to these results (33).

Silver production would depend not only on milling capacity but also on the number of available amalgamation vats, called *cajones*, with a capacity each of 50 *quintales* of amalgamation mix. Cold amalgamation could require up to 25 days, but use of a heated *cajón* could reduce this to 6 days (34). Table 3 indicates how many *cajones* would be needed to handle the maximum milling capacity

Table 3. *Cajones* required to process milled ores

total amalgamation batches (per year)	65,020	in water mills
	2,790	in horse mills
At 25 days per batch	15	batches per *cajón* per year
At 6 days per batch	60	batches per *cajón* per year
total *cajones* at 25 d	4,520	
total *cajones* at 6 d	1,130	

Each batch in a *cajón* corresponds to 50 *quintales*

of the *Ingenios*. An anonymous report from Potosí dated 1603 mentions the existence of 60 thousand *cajones*, greater than the requirements estimated in Table 3 (35). Based on this report the physical bottleneck in production would have been the installed milling capacity and not the number of available *cajones*.

How much of this plant capacity could have been destined for producing contraband silver? As Table 4 shows, it depends on the silver content of the ore being processed. Capoche provides information on a variety of ores of the period, and I have chosen to calculate the values in Table 4 from the lowest range of 2 pesos per quintal (0.12 % by weight of silver) to 8 pesos per quintal (0.49%) (36). The level of potential contraband depended on how much capacity is freed as the silver content of the ores increases. At the high end of the scale, if ores were being processed that had an average silver content of 8 pesos per *quintal*, only 25% of the installed capacity was required to produce the levels of silver reported in

the official data, and the remaining 75% could be used to produce contraband silver. Even at a silver content of 4 pesos per *quintal* half the plant could be dedicated to refining contraband silver. This means that the estimated ranges reported in the historiography of 1 to 1 or 2 to 1 contraband to official silver production (Ref. 3) could in principle be accommodated by the existing plant capacity in 1585. Only with the ores poorest in silver (2 pesos per quintal) could it be said that the installed capacity was in line with official production data.

As the silver content of the ore and the total processing capacity of the *Ingenios* decreased over time (the number of *Ingenios* is reported as dropping from a high of 132 to a low of 34 in 1692 (37)), official silver production figures would have come closer to the nominal capacity of the installed infrastructure required to process ore and extract silver.

Comparison to Other Estimates of Contraband in Potosí

Bakewell discussed at length the possible impact of contraband in Potosí both on production trends and on the mercury to silver weight ratio. He concluded that the impact on the former might lead to more pronounced decreases but that it would be difficult to arrive at any solid conclusion based just on the shape of the production curve over time. His analysis of the significance of the mercury to silver weight ratio is hampered by the fact he did not recognize that the ratio was not an empirical factor but that it has a chemical underpinning which defines the possible interpretations to its low or high values. In an amalgamation process other than the *beneficio del hierro* or the *beneficio de cazo*, the consumption of mercury by a silver ore is not determined by whether it is rich or poor in total silver content, but whether it is rich or poor in native silver (7). He concludes that based on the empirical values of the ratio as derived from the official registered data there is no evidence of any major amount of contraband taking place, since these values

Table 4. Installed silver production capacity circa 1585.

total *quintales* of milled ore for 200 days	silver in ore (pesos per *quintal*)[a]	potential silver production (pesos)	potential silver production (marks) at 8 pesos to 1 mark	average official yearly silver production 1581 to 1590 (marks)[b]
3,390,400	2	6,780,800	847,600	760,771
	4	13,561,600	1,695,200	
	8	27,123,200	3,390,400	

Sources:
a) Ref. 19 (Capoche), 78-79.
b) Ref. 3 (Bakewell), 92.

correspond very well to the lower *correspondencia* value of 150 marks to the quintal quoted in the technical audit of 1588. He considers that smelting was not important after the 1580s. He dismisses any possibility of major quantities of contraband mercury being available to produce silver (38).

The weight of his argument against any significant production of contraband silver relies on the fact that a very good correlation is observed between the *correspondencia* factor and the historical mercury to silver weight ratios for the period 1593-1686. The fact this correlation exists only means that the empirically derived *correspondencia* factor corresponds, as it should, to the factor predicted by the chemistry of the most widely used amalgamation process during the period. It does not mean that no contraband was possible during this period.

Noejovich more recently carried out an analysis of the magnitude of contraband in Potosí based also on the mercury to silver weight ratio. He detects a peaking in the level of mercury consumption around 1640-1650 where the mercury to silver weight ratio increases beyond the previous historical levels. He concludes that this would indicate an increase in the contraband production of silver during this period (39). He repeats the assumption in the historiography that a value of unity of the weight ratio represents the chemical losses and the rest the physical loss, but he does not provide any chemical background to sustain this assumption, which in any case is incorrect as a generalization. My own analysis coincides with his appreciation that the values of the ratio towards the 1640s and 1650s indicate a higher consumption of mercury, most probably due to mercury being diverted to producing contraband silver under the guise of a higher *correspondencia* factor.

Conclusions

I have tested two approaches to detect and quantify contraband of silver during the period 1576-1650 coming out of the two main silver production centers of this period in the Vice-Royalty of Peru, Potosí and Oruro. I have first analyzed the variations of the mercury to silver weight ratio on the basis it is a factor determined by the stoichiometry of the reduction of silver chloride to elemental silver and the production of calomel from mercury, together with the extent of physical losses of mercury during amalgamation. Since it does not depend on absolute production levels it is not influenced by factors that affect production and that could be confused with contraband (40). Its limitation is that to calculate the ratio requires information from the official records. If these were altered according to the expected correlation (*correspondencia*) between mercury consumption and silver extraction then its utility to detect contraband becomes more limited. The range of mercury to silver weight ratios from 1576 to 1650 only indicate a higher than average use of mercury from 1630 to 1650, which could be due to increased contraband activity. The ratio does not register any lower values than expected except in the decade 1601 to 1610, where the effect of the *Beneficio del Hierro* created a glut of mercury in the distribution system.

The second approach involves the estimation of the nominal production capacity for a refining center, and therefore has the advantage that it does not rely on any set of production data, either of mercury or of silver. This freedom from possible biases introduced in the official tax record makes it a very valuable method if the information on the infrastructure is available. The richer the ore, the wider is the gap between the potential refining output and the official silver production data for the Potosí refining infrastructure of 1585. The existing plant capacity could refine up to twice more silver than appears in the official production data, if sufficient contraband mercury was available. A similar exercise carried out on

the nominal capacity of the physical infrastructure that existed in Huancavelica for the production of mercury during this period is required to complete the picture.

The implications of such potential contraband reach beyond the sphere of economic history. Already the official record of mercury production points to average yearly losses of nearly 500 tons of mercury as calomel and as elemental mercury in the Hispanic New World for over 250 continuous years. How much more was actually lost as a consequence of the production of contraband amalgamated silver remains to be established.

Acknowledgment

References and Notes

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3. An estimate of one third official production to two thirds contraband silver towards the end of the colonial period is quoted from *El Mercurio Peruano* of 1793 in P. Bakewell, "Registered Silver Production in the Potosí District, 1550-1735," *Jahrbuch für Geschichte Lateinamerikas,* **1975**, *12*, 67-103 (see p. 80); contraband as half of total silver output in Peru, see footnote 27 in D. O. Flynn and A. Giraldez, "Cycles of Silver: Global Economic Unity through the Mid-Eighteenth Century," *Journal of World History*, **2002**, *13*, 391-427 (see p. 404); for silver contraband estimates in the trade between the Vice-Royalty of Peru and New Spain, with official exports around 50 to 80% of real total silver exported in this route, see D. O. Flynn and A. Giraldez, "Arbitrage, China and World Trade in the Early Modern Period," *Journal of the Economic and Social History of the Orient*, **1995**, *38*, 429-448 (see p. 435).

4. Ref. 2, 439.

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7. S. Guerrero, "Chemistry as a Tool for Historical Research: Identifying Paths of Historical Mercury Pollution in the Hispanic New World," *Bull. Hist. Chem.*, **2012**, *37*, 61-70.

8. Ref. 6, 175.

9. Some of the best visual depictions of the concatenated operations involved in the industrial-scale refining of silver ores in Potosí can be found in the engravings that accompany the work by B. Arzáns de Orsúa y Vela, *Historia De La Villa Imperial De Potosí*, L. Hanke, and G. Mendoza L. (Eds), Brown University Press, Providence, 1965.

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12. M. Jiménez de la Espada, *Relaciones Geográficas de las Indias - Peru*, Vol. II, J. U. Martínez Carreras (Ed.), Biblioteca de Autores Españoles, Tomo 184, Editorial Atlas, Madrid, 1965. Instructions of the Vice-Roy Don Fernando de Torres y Portugal to Juan Ortiz de Zárate as quoted on p. 121.

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18. Ref. 3 (Bakewell), 82.

19. L. Capoche, *Relación General de la Villa Imperial de Potosí*, Biblioteca de Autores Españoles, Tomo 122, Ediciones Atlas, Madrid, 1959, 178; Ref. 3 (Bakewell), 74-80; Ref. 6, 181-186. Bakewell indicates that the records for Zacatecas in New Spain up to the 1700s contain information as well on the marks of silver produced.

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21. W. E. Rudolph, "The Lakes of Potosí," *Geographical Review*, **1936**, *26*, 529-554; see 537.

22. Ref. 3 (Bakewell), 94.

23. The same conclusion is reached, albeit without any calculation of mercury to silver weight ratios or a chemical explanation to sustain it, in Ref. 2, 133.

24. "*La invención del hierro ... no se les sacaba mucha plata, [pero] no se perdía azogue*" in an anonymous document titled "Descripción de la Villa y Minas de Potosí. Año de 1603," as reproduced in M. Jiménez de la Espada, *Relaciones Geográficas de las Indias - Peru*, Vol. I, J.U. Martínez Carreras (Ed.), Biblioteca de Autores

Españoles, Tomo 183, Editorial Atlas, Madrid, 1965, 375. All translations by the author. For a discussion of the chemistry see Ref. 7.

25. "Thanks to the discovery this year 603 [*sic*] of amalgamation using lime, it has been possible to use less iron, since previously no less than 4 thousand *quintales* of iron were consumed every year." ("*Con la ocasión que este año 603 ha habido en el descubrimiento del beneficio de la cal, es ocasión de que no se gaste tanto hierro como solía, pues no había año que no se gastasen 4 mill quintales de hierro*." Anonymous, Ref. 24, 383.)

26. Ref. 2, 156, 178, 453.

27. M. B. Abbott and A. P. Wolfe, "Intensive pre-Incan Metallurgy Recorded by Lake Sediments from the Bolivian Andes," *Science*, **2003**, *301*, 1893-1895; see 1894. All years in the text are to be understood as being Common Era.

28. Ref. 10, 188.

29. Ref. 19 (Capoche), 118-122; other data from Ref. 11, 86-89.

30. Taking into account sixteenth century technology, water restrictions and a remote site such as Potosí, a plant operating factor of 55% may be a realistic level with potential to increase output subject to economic incentive and available ore and mercury.

31. Ref. 19 (Capoche), 164.

32. Anonymous, Ref. 24, 379, 383.

33. Ref. 11, 86-89.

34. Ref. 19 (Capoche), 123.

35. Anonymous, Ref. 24, 384.

36. Ref. 19 (Capoche), 78-79.

37. J. A. Cole, *The Potosí Mita:1573-1700: Compulsory Indian Labor in the Andes*, Stanford University Press, Stanford, 1985, 47. Even though a decrease in number could be compensated by an increased capacity of the remaining ones, the sharp drop reported is expected to have decreased the overall processing capacity for silver ores at the end of the seventeenth century.

38. Ref. 3 (Bakewell), 80-86.

39. H. O. Noejovich, "El consume de azogue: ¿Indicador de la corrupción del sistema colonial en el Virreinato del Perú? (Siglos XVI-XVII)," *Fronteras de la Historia*, **2002**, 7, 77-98.

40. Copper *magistral* would make the recipe more efficient, since copper sulfide is converted into silver chloride, and thus more silver is extracted from the ore, but it would not change the underlying weight ratio of mercury to silver that is determined by the stoichiometry of the reduction by mercury of silver chloride to elemental silver and calomel. It can be argued that ores difficult to treat, for example the *negrillos*, increase the possibility that more mercury will be lost mechanically. The range of historical *correspondencia* values corresponds to a range of physical losses of 0.05 to 0.1% per amalgamation cycle. See Ref. 7.

About the Author

Saúl Guerrero received his degree in Chemistry at the Universidad Simon Bolivar (Venezuela) in 1975 and a Ph.D. in Polymer Physics from Bristol University (UK) in 1980. After a career of teaching and research in the area of polymers and then as an international marketing manager for a major oil company, he obtained an M.A. in Global History at the University of Warwick (UK) in 2009 and is at present a Ph.D. candidate in the History Department of McGill University thanks to the award of a Peter Cundill Fellowship.

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JOHN WILLIAM BAKER AND THE ORIGIN OF THE BAKER-NATHAN EFFECT

Martin D. Saltzman, Providence College, msaltzmn@providence.edu

The Baker-Nathan effect was a theory proposed by John William Baker (1898-1967) and Wilfred Samuel Nathan (1910-1961) of Leeds University in 1935 to explain certain anomalous results obtained in SN_2 reactions carried out in solution. The explanation produced by them was expanded to a general type of no-bond resonance known as hyperconjugation by Mulliken in papers published in 1939 and 1941 (1). Hyperconjugation is today defined as the conjugation of polarized sigma bonds and adjacent pi orbitals. This theory has been applied to a host of anomalous physical measurements such as bond lengths and dipole moments. The Baker-Nathan effect as it was originally framed is no longer used in light of more plausible explanations for rate accelerations in solution.

This paper will first deal with the life of John William Baker, a name that is far from familiar to most chemists today. Those chemists who received their training in physical organic chemistry in the pre-1975 era probably remember the Baker-Nathan effect. The paper will then examine how Baker and his collaborator Nathan discovered what was believed to be the first example of hyperconjugation. Next it will briefly discuss the downfall of the Baker-Nathan effect as an explanation of what happens in unexpected rate accelerations in reactions in solutions. A brief discussion of the concept of hyperconjugation as used today will conclude this paper.

John William Baker

John William Baker was born in London on March 10, 1898, and he attended the Latymer Upper School, an independent school in west London from 1909-1916. He was awarded a Royal Scholarship in Chemistry which allowed him to enroll at the Imperial College of Science and Technology in London. His exceptional aptitude for chemistry was shown by his passing the intermediate exams for the B.Sc. Degree by the end of 1916. In April 1917 he was conscripted and assigned to the Royal Engineers where he was commissioned a Lieutenant. His major responsibilities were in the area of water purification. In May 1918 he was sent to Mesopotamia (now Iraq) where he was assigned the same duties. He was finally demobilized in 1920 and returned to Imperial where he was awarded his B.Sc. with first class honors in 1921. The M.Sc. was awarded in 1923, a Ph.D. in 1925 and D.Sc. in 1928. His dissertation was nominally supervised by Jocelyn W. Thorpe (1872-1940) (2) but most directly by Christopher K. Ingold (1893-1970) (3).

Jocelyn Thorpe worked in the laboratory of Victor Meyer in Heidelberg under the guidance of Karl von Auwers. He was awarded his D.Phil. in 1895 and then assumed a junior position at Owens College in Manchester under W. H. Perkin Jr. (1860-1929). In Manchester in addition to his teaching duties he worked on a variety of synthetic organic problems. He stayed until 1909 when he was awarded the Sorby Research Fellowship at the University of Sheffield. Freed from any teaching or administrative duties, he was able to produce a large body of research which led in 1913 to his being offered the professorship in organic chemistry at Imperial College.

In Thorpe's first year at Imperial, Ingold, after completing undergraduate studies in Southampton joined his

research group and quickly established himself as both a first class researcher and an innovative thinker. As part of the war effort Ingold was involved in the production of tear gas and other related work at the Cassel Cyanide company in Glasgow. When the war ended there seemed little possibility of Ingold entering the realm of academia and so he stayed at Cassel for another two years. In 1920 Thorpe was able to secure Ingold a position as a lecturer in organic chemistry at Imperial. In the postwar years there were two major research programs that Thorpe carried on with the assistance of Ingold: the effect of alkyl substitution on ring closure, which led to the Thorpe-Ingold principle, and ring-chain tautomerism.

Baker was supervised by Ingold and the two papers he jointly published with Thorpe and Ingold reflect this program. The first was in 1923 and dealt with ring closure, and the second in 1924 was concerned with ring-chain tautomerism (4). In 1925 the possibility of a university position of any sort for Baker was bleak to say the least. As a matter of necessity he accepted the position of Senior Chemistry Master at the North-Eastern County School in Barnard Castle in the northeast of England. However his days as a schoolmaster were very brief due to the meteoric rise of Ingold in British chemistry. At the unheard-of age of 30, Ingold was elected a Fellow of the Royal Society and was offered the professorship at Leeds University vacated by the retirement of J. B. Cohen (1859-1935).

Ingold was allowed to pick his own staff and he assembled a first class group of investigators as junior members. Baker was hired as an assistant lecturer, and the group grew to have several future notables in British chemistry such as Harold Burton (1901-1966) and Charles W. Shoppee (1904-1994). During Ingold's brief six-year tenure at Leeds which lasted until 1930 when he left for University College London, there were three ongoing areas of research. The first was aromatic substitution and the mechanism of aromatic side-chain reactions. The second dealt with aniontropic change, which was part of his continuing interest in the ionic mechanism of tautomerism. The third research program dealt with the effects of polar substituents on the velocity and orientation in addition reactions to unsaturated systems.

Baker published six papers during the Ingold time at Leeds. Three of these dealt with the nature of the alternating effect; one involved ring-chain tautomerism; and two involved ring formation (5). These were sufficient for him to be awarded the D.Sc. degree by University of London in 1928. Baker was never involved in the ongoing

acrimonious debate that occurred between Ingold and Robinson concerning the application of the electronic theory to aromatic substitution in the late 1920s.

In 1930 Robert Robinson resigned his professorship at University College London to become the Waynflete Professor of Organic Chemistry at Oxford. Ingold was offered the position Robinson vacated, and he immediately accepted the chance to return to London from Leeds, which in the 1920s was a very grimy industrial city with very unhealthy air quality. The conditions of Ingold's employment at University College would not let him bring any of his team with him. The only person who did go to London was Christopher L. Wilson who was finishing his B.Sc. and wished to do his Ph.D. under Ingold at University College. Ingold was strongly in favor of Baker becoming his successor at Leeds (6) but the professorship went instead to Frederick S. Challenger (1887-1983), a natural products chemist from the Univeristy of Manchester. Challenger had joined the staff in Manchester in 1920 and had worked with Robinson. Baker, Shoppee, and Burton among others were in Shoppee's words "left high and dry in the provinces" (7). Challenger had no problem with Baker continuing his line of research in physical organic chemistry. Baker would remain at Leeds for the balance of his academic career, ultimately becoming the Reader in the Mechanism of Organic Reactions. He did apply for several professorships during his time at Leeds. In 1943 he was considered for the professorship at University College, Bangor, but the appointment was given to Edward D. Hughes instead. Baker was never elected a Fellow of the Royal Society either, which was surprising given his research output and the difficult circumstances in which this research was conducted, namely economic depression, war, and post-war austerity.

In his career Baker published over 100 papers of which 76 appeared in the *Journal of the Chemical Society*. In 25 of his *J. Chem. Soc.* papers he was the sole author. In addition he was the author of four monographs and books. These were *Natural Terpenes* (1930) (8), *Tautomerism* (1934) (9), *Hyperconjugation* (1953) (10), and *Electronic Theories of Organic Chemistry* (1958) (11). His *Hyperconjugation* has the following dedication in the preface: "To Christopher Kelk Ingold in grateful appreciation of his inspiring friendship throughout my career."

When Ingold left Leeds in 1930 Baker took over his teaching duties in the first-year organic chemistry course. His approach followed that of Ingold and in essence he was Ingold's man in the northeast of England

Figure 1. Group photo from Baker's time at Leeds

for the physical organic approach to organic chemistry rather than repetition of endless facts with no obvious connection which was so typical of the time. However Baker's reverence for Ingold caused him to ignore other important changes that were going on, and his course did not substantially change in content for over 27 years. What was revolutionary in 1930 was dated by 1957 when the newly appointed professor of organic chemistry Basil Lythgoe removed Baker from the course. This was not taken very well by Baker, who resigned in 1959 ostensibly because of the ill health of his wife. When his wife died in 1962 he moved to York where his only child, a son, lived. He remarried and became very active in the Congregational church, devoting his final years to church work. He died on May 12, 1967.

Wilfred Samuel Nathan was born in December 1910 in Cardiff, the son of parents who immigrated to Wales from the continent. He obtained his Ph.D. at University College, Bangor, under the supervision of the noted physical organic chemist Herbert Ben Watson in 1935. With support from a Department of Scientific and Industrial Research grant he was able to work with Baker in Leeds for one year. When this grant expired Nathan moved to Ingold's group at University College London where he was supported by a grant from Imperial Chemical Industries. In 1936 he accepted a position with British Petroleum (BP) at their laboratory in Llandarcy, Wales. He was transferred in 1941 to BP's facility at Sunbury-on-Thames near London and spent the rest of his professional career there. At BP he worked in a variety of areas including thermal diffusion, the behavior of waxy crude oils and

Figure 2. Nathan's photo from his obituary from the BP Shield

the mechanism of wear in engines. He died on August 6, 1961, from complications following surgery.

How the Baker-Nathan Effect Was Discovered

In a paper published in 1935 in the *Journal of the Chemical Society* bearing the title "The Mechanism of Aromatic Side-chain Reactions with Special Reference to the Polar Effects of Substituents. Part V. The Polar Effects of Alkyl Groups," (12) we find the first discussion of what came to be known as the Baker-Nathan effect. This paper was a study of the Menschutkin reaction between *p*-substituted benzyl bromides and pyridine in dry acetone. This is an example of a class of SN_2 reaction where the reactants are both neutral. The results did not conform to the usual order of reactivity expected. Ingold had discussed the effect of alkyl substituents on SN_2 reactions in terms of the positive inductive effect (+I) at a saturated carbon atom. Thus one would expect that the order of alkyl groups based on electron releasing abilities would be *t*-Bu > *i*-Pr > Et > Me > H. This had been experimentally proven to be the case in several studies done prior to 1935. The experiments undertaken by Baker and Nathan introduced a new scenario in that the alkyl group was part of a conjugated system. To rationalize their results Baker and Nathan contemplated the possibility that a resonance effect or mesomeric effect to use Ingold's terminology was also operating in this case in addition to the inductive effect.

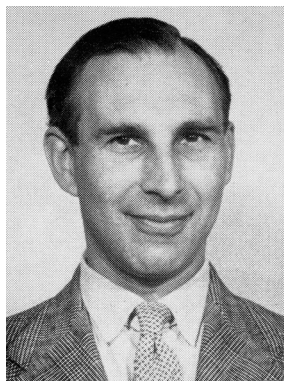Ingold in his 1934 *Chemical Reviews* paper "Principles of an Electronic Theory of Organic Reactions"

(13) discussed the various types of electronic effects that could occur to explain the mechanisms of organic reactions. Baker and Nathan used the Ingold nomenclature as the basis to explain the anomalous behavior of the methyl group (12):
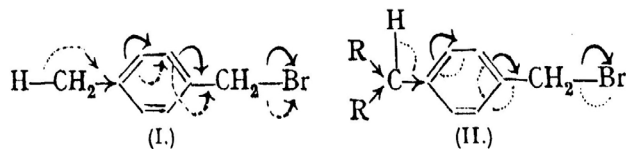
> It is tentatively suggested that, *when the methyl group is attached to a conjugated system* [italics in original], the duplet of electrons forming the C–H bond in this group are appreciably less "localized" than are those in a similarly placed C–C bond. This means that a methyl group, attached to the necessary system, is capable of permitting electron-release by a mechanism which, in essentials, is a type of tautomeric effect,
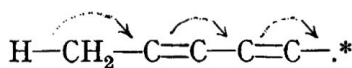
The asterisk refers to a note at the bottom of the page which reads as follows: "The original suggestion that such a polar effect is present was due to W. S. N."

How Nathan came up with the idea we do not know but considering that Nathan was a relatively young man and had been a student in the early 1930s when both valence bond theory and molecular orbital theory had been developing, he may have been influenced by these new ideas. The caveat was made that this new effect was in addition to the normal positive inductive effect (+I) of alkyl groups.

The rationale that was presented by Baker was that if methyl increased the rate of SN_2 reaction in benzyl systems and *tert*-butyl had the least effect this must be due to the lack of what came to be known as hyperconjugation. When a conjugated system is not present, then the normal inductive effect occurs and the rates are reversed. This argument can be clearly seen in the following diagram included in the text. The ordinary inductive effect is in-

dicated by fully pointed arrows and the hyperconjugative effect by the dotted arrows.

This new effect was used by Baker and Nathan in the same paper to explain the Hofmann degradation reaction of quaternary ammonium hydroxides. When ethyl dimethyl propylammonium hydroxide is subjected to the Hofmann degradation reaction it produces ethylene as predicted. Baker and Nathan offered an explanation which invoked their newly discovered effect. The key to the path of the reaction is which of the hydrogen atoms

is removed by the hydroxide ion. As the C–H bond is being broken and negative charge is being built up, as in the case of the propyl group, the inductive effect of the methyl will intensify the negative charge and retard this hydrogen being lost. The ethyl group operates in such a way as to minimize the inductive effect and hyperconjugation will facilitate the breakage of the C–N bond to the ethyl group and the formation of the double bond in ethylene. These effects are illustrated in the following diagram from Baker and Nathan's paper (12).
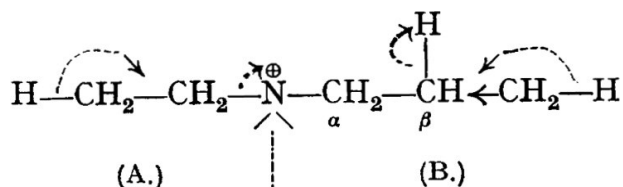

A further question that needed to be answered was whether the effect was, using the Ingold terminology, strictly a mesomeric effect (a permanent polarization effect also known as the resonance effect) or one that is an electromeric effect (a polarizability effect caused by an attacking reagent). In order to answer these questions Baker, Nathan, and Shoppee conducted a study "The Effects of *p*-Alkyl Substituents on Prototropy in the Methyleneazomethine System" (14). Prototropy is a special case of the general phenomenon of tautomerism, a subject that Baker was very familiar with from his previous work with Ingold and Thorpe.

Shoppee had shown in 1931 (15) that this reaction was favored by electron-withdrawing substituents (negative inductive effect, –I). These new studies of tautomerism in the azomethine system involved alkyl substituents only in the para position. Any alkyl group would be expected because of its +I (positive inductive
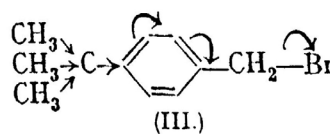
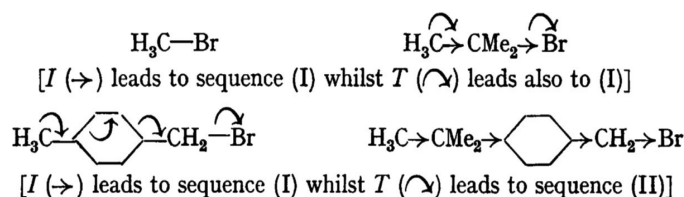effect) to slow the rate of reaction as compared to the parent system. If the methyl group interaction involved a mesomeric (resonance) effect (as in the diagram from Ref. 14) then it would be expected to retard the reaction to a greater extent than the *tert*-butyl group. This indeed is what was observed in the experiments performed.
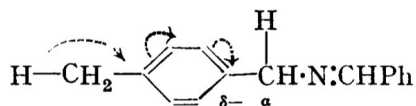
There was still a lack of a clear-cut experimental

result which could show in a definitive manner that hyperconjugation was a real effect and not the result of some already known factor. Hughes, Ingold, and Taher tackled this question in a paper "Mechanism of Substitution at a Saturated Carbon Atom. Polar Effects in Alkyl Groups, as Illustrated by Solvolytic Substitutions of *p*-Alkylbenzhydryl Chlorides," published in 1940 in the *Journal of the Chemical Society* (16).

These investigators point out that in the displacement reactions in a series of simple alkyl bromides, the Baker-Nathan effect would operate in the same manner as the inductive effect. Thus it would be impossible to see if the effect is a real one. However, in the reactions of a *p*-alkyl benzyl bromide series, although the inductive effect and the tautomeric effect (Baker-Nathan) would reinforce one another, the order of reactivity would be different depending on which effect predominated. Not knowing whether the inductive effect or the tautomeric effect would be the most important, one would have difficulty in predicting the order of reactivity. If the Baker-Nathan effect is not real or is real but very weak, then the predicted order of reactivity would be Me < Et < *i*-Pr < *t*-Bu (sequence I in the following figure taken from Ref. 16), but if the Baker-Nathan effect is real and dominant, the order would be H < {Me > Et > *i*-Pr > *t*-Bu}.

H_3C—Br

$H_3C \rightarrow CMe_2 \rightarrow Br$

[*I* (→) leads to sequence (I) whilst *T* (⤻) leads also to (I)]

$H_3C \diamondsuit CH_2$—Br

$H_3C \rightarrow CMe_2 \rightarrow \langle \rangle \rightarrow CH_2 \rightarrow Br$

[*I* (→) leads to sequence (I) whilst *T* (⤻) leads to sequence (II)]

The original report of the Baker-Nathan effect (12) was based on the study of an SN_2 reaction in a series of compounds that did not give rise to large variations in the rates of reactions. For example, the difference between H and Me where one would expect both an inductive and tautomeric (hyperconjugative) effect was only 1: 1.65. As Ingold and his co-workers put it, "It is impossible to be confident that so closely spaced a rate series means what it may appear to mean" (16).

They explains the rationale for the study they are about to describe as follows (16):

> What we need in order to get over the difficulty revealed in all this work is a device for making *one* of the four contributing factors (and it must be one of the two which involves alkyl conjugation) much greater than all others; and this can be done. We decide [*sic*] to study reaction rate in a *strongly*

electron-demanding reaction, and there can hardly be any reaction more suitable than a *unimolecular* nucleophilic substitution, where there is only a single electron-transfer involving carbon in the rate-affecting stage. [italics in original]

The reaction that was chosen for study was the hydrolysis of *p*-alkylbenzhydryl chlorides in 80% aqueous acetone, a reaction known to be of the SN_1 type. If the Baker-Nathan effect was real then there would be a competition between the inductive effect and the conjugative Baker-Nathan effect. The key would be in the transition state where the conjugative effect would be paramount in lowering the energy of activation by electron transfer.

The results obtained by Hughes, Ingold and Taher (Table 1) were consistent with the order that would be predicted if the Baker-Nathan effect existed. This order was H < Me > Et > *i*-Pr > *t*-Bu. In addition to the large rate increase for Me vs H, all the other alkyl groups showed decreases with respect to Me in a regular manner as would be predicted by reduced hyperconjugative ability. "We regard this as the first satisfactory *evidence* of the reality of alkyl conjugation as envisioned by Baker and Nathan" (16).

Table 1. First-order Rate Constants and Arrhenius Parameters for the Hydrolysis of Benzhydryl Chloride and its *p*-Alkyl Derivatives (Table I of Ref. 16)

p-Substituent	H	Me	Et	*i*-Pr	*t*-Bu
$10^6 \, k \, (s^{-1})$ at 0.0°C	2.82	83.5	62.6	46.95	35.9
$10^{-11} \, A \, (s^{-1})$	1.91	1.23	2.19	3.47	4.07
E (kcal mol^{-1})	21.0	18.9	19.4	19.8	20.05

One further paper published by Baker in 1942 (17) should be mentioned. This dealt with the reaction of aldehydes to produce cyanohydrins as evidence for the mesomeric (hyperconjugative) effects of alkyl groups. Baker performed these studies to add further experimental evidence for the rate enhancement by methyl in contrast to *tert*-butyl when something other than the inductive effect is at work. Lapworth (18) had previously shown that in the equilibrium between *p*-substituted

$H \rightarrow CR_2 \diamondsuit CH=O$ + HCN $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$ $H \rightarrow CR_2 \diamondsuit CH(OH)\cdot CN$
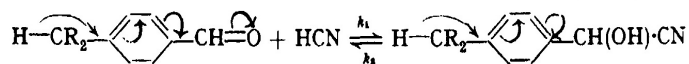
benzaldehydes and their cyanohydrins that electron-releasing groups stabilized the aldehyde and destabilized the cyanohydrins. Baker studied the series of *p*-alkyl benzaldehydes where hyperconjugation was possible in the aldehydes but not in the cyanohydrins. He found that

the order of stability of the cyanohydrins with respect to their corresponding aldehyde was in the order H > *t*-Bu > *i*-Pr > Et > Me. It thus seemed that hyperconjugation was a real phenomenon.

Chemists increasingly used the Baker-Nathan effect to provide explanations for unusual patterns of rate enhancements and equilibrium as well as physical measurements such as bond lengths, dipole moments, and heats of hydrogenation to name a few. Two reviews of hyperconjugation were published in 1945 in *Chemical Reviews* (19) and in 1949 in *Quarterly Reviews of the Chemical Society* in 1949 (20), which gave an overview of how this effect was used to explain certain anomalies.

Table 2 lists references made to the Baker-Nathan effect and hyperconjugation in some popular texts of a more advanced nature published from 1943 to 1974. This is by no means a comprehensive listing, but it does provide evidence that the concept of hyperconjugation was taken seriously as a means of explanation in the chemical community.

In addition popular undergraduate textbooks such as Morrison & Boyd and Streitwieser & Heathcock of this period also mentioned the role of hyperconjugation as an explanation for certain anomalous experimental findings (22).

What Happened to the Baker-Nathan Effect?

Today the Baker-Nathan effect is an historical footnote remembered by those who received their training in physical organic chemistry prior to the mid-1970s. During the mid-1950s there was great enthusiasm for using the Baker-Nathan effect as a way of explaining unexpected results when inductive effects were thought to be the driving force behind reactivity. One of the first to challenge this explanation was a paper published by Schubert and Sweeney in 1956. This paper with the in-

nocent enough title of "Concerning the Baker-Nathan Effect" offered an explanation based upon solvent effects (23). In this investigation of *p*-alkylbenzhydryl chlorides in 80% aqueous acetone it was shown that if the same reaction is carried out in the gas phase the order of reactivity was reversed with methyl now showing the least reactivity. Since the structure of the reactants was exactly the same the difference must be due to solvation effects and not to hyperconjugation in this case (23):

> It should be made clear that the position being taken is not that C–H hyperconjugation is necessarily of no consequence, although the concept is not needed to explain the data cited here. The viewpoint is simply this: if the role of the solvent as discussed is of importance then other modes of electron release by alkyl groups in the order *tert*-Bu > Me may be relatively more important, even when attached to an electron-demanding system.

This paper did not mark the beginning of a decline in the appearance of the Baker-Nathan effect in the chemical literature. Indeed, Schubert and Sweeney appear to have inspired a number of studies of solvent effects in connection with the Baker-Nathan effect. A search of SciFinder for the topic "Baker-Nathan" shows more papers from the 1960s than any other decade and that about 1/3 of papers dealing with "Baker-Nathan" were papers published after 1956 and also concerned with solvents (24). Invocation of the Baker-Nathan effect in the chemical literature has dropped to practically nothing over the last 30 years, and some of those few papers that continue to treat it also continue to investigate the extent to which it can be attributed to solvent effects. For example, Conney and Happer looked at chemical shifts in ^{13}C NMR in alkyl-substituted styrenes. They found that the order of substituent effect did not change in a variety of solvents ranging from non-polar to polar aprotic to polar protic, a result they interpreted as hyperconjugative because the solvent seemed not to matter much (25). Ten years later,

Table 2. Hyperconjugation references in some texts from 1943-1974 (21).

Text author and title	Year of publication	Number of pages devoted to hyperconjugation
Remick, *Electronic Interpretation of Organic Chemistry*	1943	10
Alexander, *Ionic Organic Reactions*	1950	8
Waters, *Physical Aspects of Organic Chemistry* (4th ed.)	1950	8
Gould, *Mechanism and Structure in Organic Chemistry*	1959	11
Fieser &Fieser, *Advanced Organic Chemistry*	1961	4
Hirsch, *Concepts in Theoretical Organic Chemistry*	1974	8

a computational chemistry paper by Exner and Böhm reported hyperconjugative stabilization in *p*-alkylbenzyl cations but not in the neutral parent hydrocarbons, concluding that the Baker-Nathan effect in solution kinetics must be a solvent effect (26).

in Figure 3 are "Ngrams," plots of the frequency of occurrence of a word or phrase in the corpus of scanned books and journals at the Google Books project (27). The plots show that even at the height of their popularity, Baker-Nathan occurred in print more than an order of magnitude less frequently than did hyperconjugation.
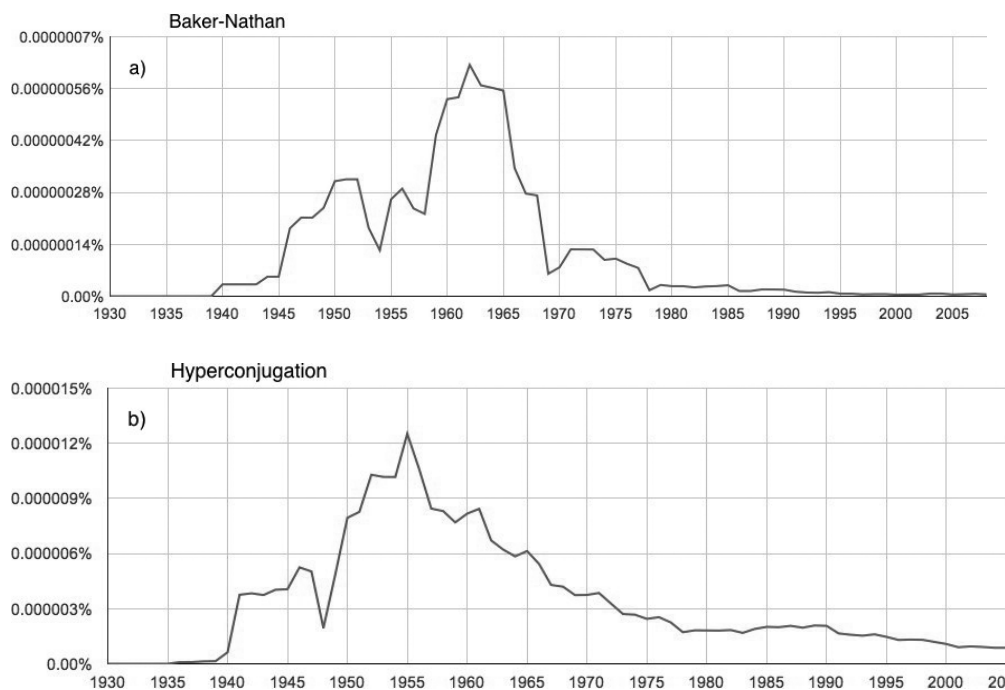
Figure 3. Ngrams for the terms (a) Baker-Nathan and (b) hyperconjugation (27).

The decline of the Baker-Nathan effect, then, does not appear to be a simple matter of displacement by a better explanation. In addition to questions about the source of the effect, other factors appear to include a restricted range of the term's usage as well as larger currents in physical-organic chemistry.

Some researchers have made a distinction between the Baker-Nathan effect and hyperconjugation, treating the latter term as a more general or theoretical concept and the former as a term of more restricted application. Exner and Böhm, for example, consider the Baker-Nathan effect as an empirical term restricted mainly to trends in reactivity (26). A related usage point can be seen in the title of Conney and Happer's paper, which refers to Baker-Nathan *order*, that is, to an empirical result (25).

Regardless of just how individual researchers have used the terms Baker-Nathan and hyperconjugation, the former was never as widely used as the latter. The graphs

Both terms have declined in frequency, which seems to suggest a move away from their subject matter in physical organic chemistry. Whereas Baker-Nathan has all but disappeared, hyperconjugation continues to appear in print.

It is difficult to be definitive, but it would seem that the disappearance of the Baker-Nathan effect from chemical literature is due to a combination of doubt over the utility of the concept in its original and rather restricted realm of application (reactivity in solution) and a shift in research interests in physical organic chemistry more widely. The concept of hyperconjugation is still used in certain contexts, and it remains a useful concept in education (28), even though the original Baker-Nathan effect has long passed into history of physical organic chemistry as a footnote. Although there is still controversy among theoreticians about hyperconjugation, Baker and Nathan as a result of their 1935 experiments opened a new way to explain many puzzling problems in organic chemistry.

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About the Author

Martin D. Saltzman is Professor of Natural Science at Providence College, Providence, RI.

THE PROCESS FOR 2,3,5-TRIPHENYLTETRAZOLIUM CHLORIDE SYNTHESIS, AN INTELLECTUAL PROPERTY SEIZED IMMEDIATELY AFTER WORLD WAR II

Michael Witty, Edison State College, Fort Myers, Florida, mwitty@edison.edu

Introduction

The efforts to win World War II included use of intelligence units whose role was to find and detain German scientists then interrogate them for information regarding military information that might help the Allies in their war aims (1). This involved identification of targets by the Combined Intelligence Objectives Subcommittee (CIOS) which were pursued by Target Forces (T-Forces) whose role was to identify and intercept German scientists (2). These activities were expanded to include purely scientific and economic targets in response to several suggestions, including, for example, from Vannevar Bush, Director of the Office of Scientific Research and Development. Many reports of civilian interest were prepared and 2,720 reports published by 1948 (3). One of the many outcomes of this was the journey of civilian doctor Stanley Hall to Elberfeld on May 19, 1945—only 11 days after the end of the war in Europe—seeking medical research information on pesticides (4). An unexpected outcome of Dr. Hall's journey was information concerning a scientific tool familiar to many botanists, use of tetrazolium salts in seed viability testing.

Georg Lakon was the academic botanist who, under the guidance of Richard Kuhn, invented the method of tetrazolium testing for determining the viability of seed stocks so that a constant number of viable seeds may be sown using a mixture of viable and dead, thereby optimizing use of land. Lakon used small amounts of various salts to optimize the method, in which viable seeds are recognized because of red color development, especially in embryo tissues. He published in German (5), and his work was only widely circulated in the west after the war (4, 6). While tetrazolium testing is a very useful procedure in the botany laboratory (7), the advance which made it a widely successful commercial test was the availability of a large-scale method for synthesizing the optimal tetrazolium salt (2,3,5-triphenyltetrazolium chloride). This method was one of the economic secrets revealed by CIOS interrogation of detained German scientists from *I.G. Farbenindustrie* at Elberfeld. Precisely how scientists were found, detained, and interrogated is unknown but it may have been a fraught process considering the times. Allied personnel may have been heavy handed, or not. German scientists may have been defiant, demoralized, or despondent, or not. The process certainly involved a great clash of cultures that is rarely seen in the conduct of science and the exchange of research results. The following translation illustrates an example of information produced by this kind of interrogation.

Methods

The source material (4) is not an interrogation transcript, but it is probably based upon interrogation of a

scientist or inventor named Leuchs and edited for clarity by CIOS agents. When the general scientific interest and value of this material was fully appreciated it was published to enhance post-war recovery of the Western Allies, along with a very great number of other chemical processes developed in Germany during the Nazi period (3). My aim was not to produce a literal translation of this record of Leuchs's work, but a description of his scientific methods. I attempted to understand what he did rather than produce a literary work (8), making up for any lack of linguistic skill by long familiarity with experimental science.

To try to identify Leuchs, I searched the USPTO database (9) for all patents where the inventor name included Leuchs and patents from 1925 to 1993 were used to draw a time line of relevant patent publications. These years were used to include men in their twenties in the 1940s who may have worked into their seventies. Patents from 1899 to 1945 were also used to include older scientists who may have been conscripted through lack of manpower. Scholarly citations for these scientists were also identified (10).

Results

The following is a translation of Leuchs's work, as described by the CIOS (4, Appendix 4). Editorial comments, for clarification and the like, appear in square brackets. Structures in the source document were simply typed in line, as shown in Figure 1, the first page of Appendix 4; however, in this translation bold italic numerals are used to designate structures.

Preparation of Triphenyltetrazolium Chloride (Tetrazolium Salt) [*1*]
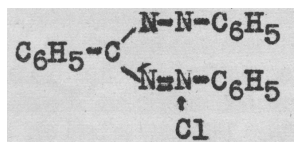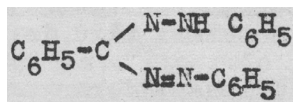
1   *2*

To 400 g triphenylformazan [*2*], 1.7 liters dry spirit and 330 [*sic*, unit omitted] amyl nitrite, mixed in a 3-liter flask with stirring, 185 g of 37% alcoholic hydrochloric acid is added dropwise. Heat of reaction causes the temperature in the flask to rise to 50-55°. When the alcoholic hydrochloric acid has been added dropwise, stirring is continued for a further 1½-2 hours; then the flask is allowed to stand without stirring for 4 hours, until no further bubble development (nitrogen) is seen. The red color of the

Figure 1. First page of Leuchs's work, as described by the CIOS (Ref. 4, Appendix 4).

triphenylformazan disappears and a deep brown solution forms. This solution is mixed with tap water until a clear oily layer (mainly amyl alcohol) separates, and about 6-8 liters of water are required. The aqueous alcoholic solution is separated by draining the oily layer and concentrated under vacuum or on a water bath to 1-1½ liters. Clarify while hot with activated carbon, and vacuum filter. Evaporate the yellowish filtrate on a water bath until the beginning of crystallization, then place on ice, so that the aqueous crude product triphenyltetrazolium chloride is obtained in solid form. For cleaning, the crude product is dissolved in hot water (to 1 part crude product add not more than 1 part water). The solution usually reacts with Congo Red, therefore it is blunted [*sic*, this sentence is not precisely clear in German or English] by 20% ammonia solution until the Congo Red acid reaction disappears (but it is still significantly acid, judged by litmus), and about 30-40 mL of ammonia solution is required. A little activated carbon is added again and the solution vacuum filtered while still warm. The filtrate is placed on ice water and

allowed to crystallize while stirring. The result is a nearly colorless triphenyltetrazolium chloride, which is vacuum filtered and dried for 2 days at room temperature, with exclusion of light, then in a steam cabinet. Triphenyltetrazolium chloride is a slightly yellow-brown crystalline powder, which decomposes at 241°, and met the required purity tests. Yield, about 300 g (67-68% theoretical yield).

Description of benzylidene-phenylhydrazone

To 108 g of phenylhydrazine and 200 mL dry spirit in a 1-liter flask add 106 g benzaldehyde dropwise, with stirring. When the benzaldehyde is added dropwise, boil 30 minutes, then cool on ice water, the benzylidene-phenylhydrazone is harvested by vacuum filtration and washed with cold dry spirit and a little ether. Drying benzylidene-phenylhydrazone is done in the light-protected desiccator [*sic*, this equipment had not been described] over calcium chloride, preferably using a water-jet vacuum. Yield 162 g, equivalent to 83% of theoretical yield. The desiccated material is transferred to brown bottles.

Description of Triphenylformazan

77 g aniline and 207 mL concentrated hydrochloric acid were diazotized with an aqueous solution of 59 g sodium nitrite, using a temperature not exceeding +10°. The diazonium solution [phenyldiazonium chloride] is filtered rapidly. During filtration or earlier, prepare a solution of 162 g benzylidene-phenylhydrazone in 350 mL pyridine fraction II [*sic*, this is a reference to an unknown fractionation method, information omitted from this document] and 350 mL dry spirit in a large beaker with stirring and cool the solution to 15-20°. Then at this temperature, add the filtered diazonium solution, dropwise with stirring. The temperature rises to about 25° when the diazonium solution is added dropwise, which does no harm. Higher temperatures should be avoided, however, by external cooling with ice. In order to prevent decomposition of the diazonium solution, set it up for use on ice water. After dropwise addition of the diazonium solution mix thoroughly for at least 2-3 hours more; the resulting red precipitate is raw triphenylformazan. Formula: [**2**]. This was vacuum filtered and washed several times with water; yield 205 g. For the purpose of further processing to triphenyltetrazolium chloride it is sufficient to boil this air-dried material with 15 parts by volume dry spirit. To this end, for example, 205 g of triphenylformazan was boiled with 3,075 mL dry spirit for 30-40 min, then left to cool overnight and finally vacuum filtered. This gives a shimmering violet crystalline product which has mp. 170-173° and is suitable for further processing. Yield: 80% of the crude product (164 g).

*Preparation of Triphenyltetrazolium Chloride (Tetrazolium Salt) [**1**]*

   . . . [iteration of all the above] . . . of the crude product (164 g).

Conclusion

It is initially surprising for a scientist used to word processors that automatically highlight spelling mistakes to see glaring typing errors (e.g. *benzaldyhd* for *benzaldehyd* and *triphenyltetrazoliumschlorids* for *triphenyltetrazoliumchlorids*) which survive all the way through the publication process. However, I became used to spelling errors, occasional omission of units and inconsistent abbreviations (e.g., "*d.Th*." and "*der Th*." for theoretical yield). There were also mistakes in chemical diagrams. Compare structures *1* and *2* above, from the detailed appendix to the summary of the synthetic scheme from the main body of the CIOS report (Figure 2). In both of the former, C–N double bonds are shown as single bonds, and in structure *1* a line indicating a C–N bond is missing. (However, note that a hydrogen atom is missing from the triphenylformazan structure in Figure 2.) I corrected some of these errors, though I have in some cases translated imperfect grammar faithfully rather than correcting it (e.g., "*mindestens 2-3 Stunden weiter*" as "at least 2-3 hours more"). The greatest error is
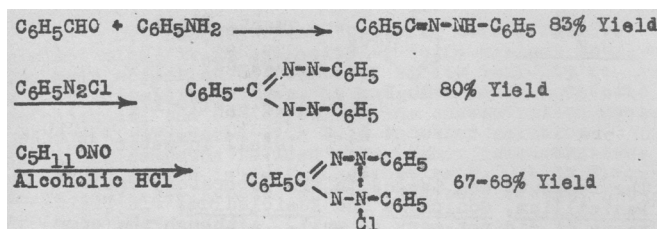

Figure 2. *Summary of Leuchs's synthetic scheme, as described by the CIOS (Ref. 4, p. 16).*

a large repetition of German text and structural formulae including imperfect copying of hyphenation, presumably of German text by an Anglophone typist (e.g., *wässrig-alkohol* contained a carriage return and hyphen in the first iteration and the hyphen was copied over so the word *wässrigalkohol* was written *wässrig-alkohol* mid page in the second iteration). I have abbreviated this large iteration and italicized the first and last few words. I have also included a summary of the synthetic scheme using more modern structural notation (Figure 3).
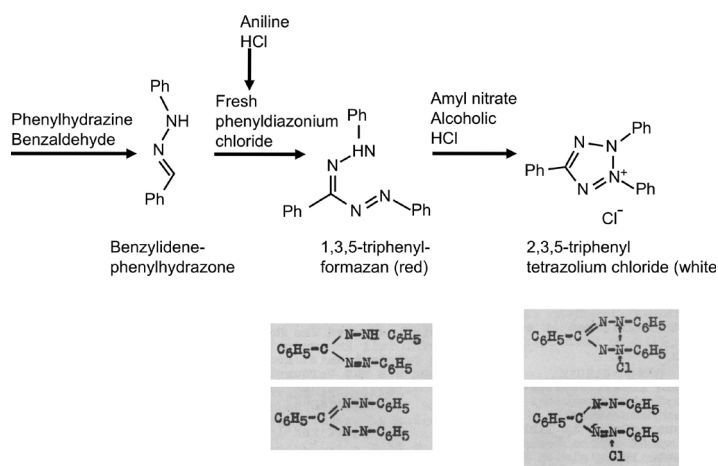
Figure 3. *Summary diagram of Leuchs's process for 2,3,5-triphenyltetrazolium chloride synthesis. Tetrazolium testing of a biological system reverses the reaction and causes 2,3,5-triphenyltetrazolium chloride (white) to revert to 1,3,5-triphenylformazan (red). Structures cited in the original text (4) are copied below the relevant structure.*

This low quality of interrogation product suggests the original documents were prepared hurriedly or the German scientists were perfunctory. After this stage the German text was not rigorously edited by a Germanophone. A reason for this may be the special circumstances under which the information was obtained; once released, the German scientists made themselves unavailable for further comment and revision of drafts became difficult. Some of the colleagues of Dr. Leuchs were certainly still not denazified at the time; for example a Dr. Mudrow still signed his written work *Heil Hitler* at this early post war phase (Ref. 4 and Figure 4). This is a translation of a slightly bizarre document that may be typical of a time dominated by administrators rather than scientists.

Precisely identifying the scientist responsible for the industrial process is difficult. I have assumed that, like most industrial scientists today, he was more interested in publishing patents than scholarly papers and it was common for *I.G. Farbenindustrie* to be assigned patents in the United States, even during the war years (though these may have been pre-war applications working their way through the system). This suggested to me that something may be learned from databases of patents. Hall (4) only cites the title and surname of the relevant scientist, i.e., Dr.

Leuchs. Taking into account the youngest possible scientist, i.e., a 24-year old doctoral graduate, this means Dr. Leuchs might have continued publishing patents for a further 41 years, until his retirement. This means patents published before 1993 are relevant; this screen limits the possible identities to six scientists (Figure 5). On the other hand, the oldest this scientist could be in 1945 is approximately 75, an old man working in desperate circumstances, and so searching scholarly databases for papers published from 1899 to 1945 was also considered relevant. Two organic chemists were found using these overlapping methods: Dieter Leuchs, a young man in 1945 and Friedrich Leuchs, an older man. Further evidence is clearly needed, though one may wonder whether
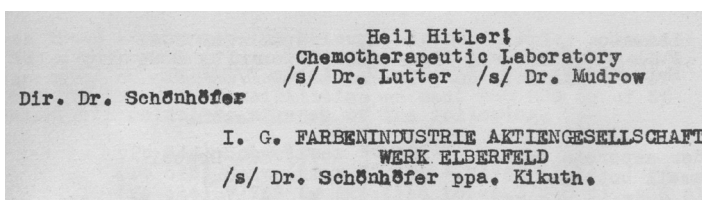

Figure 4. *Transcript of signatures from Appendix 3 of Ref. 4, "Results of Testing Repellents and Mosquitocides."*
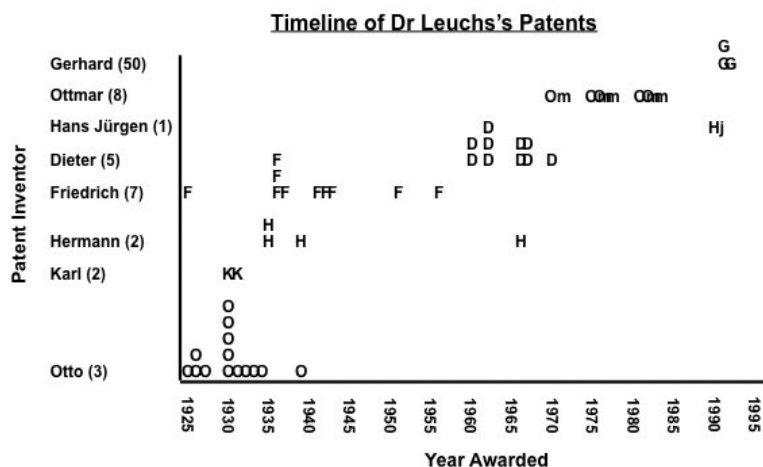
Figure 5. *The following US patents were used to compose this graph: 1,558,375; 1,583,717; 1,588,758; 1,640,506; 1,694,127; 1,746,663; 1,755,657; 1,766,822; 1,767,382; 1,767,382; 1,770,412; 1,814,208; 1,853,626; 1,871,868; 1,913,478; 1,982,760; 2,004,545; 2,020,713; 2,086,585; 2,087,131; 2,087,132; 2,113,606; 2,168,167; 2,172,076; 2,229,810; 2,305,297; 2,336,179; 2,650,943; 2,856,471; 2,951,847; 2,954,370; 3,082,114; 3,086,002; 3,108,104; 3,232,928; 3,255,173; 3,297,679; 3,314,934; 3,329,710; 3,498,735; 3,698,440; 3,943,087; 4,008,368; 4,297,526; 4,345,363; 4,952,730; 5,124,994; 5,172,185; 5,177,566. The inventor's initial or two initial letters were used to define data points. The number of relevant scholarly citations for each scientist is in brackets.*

the scientist interrogated in 1945 was an older man who lived to see his nation defeated a second time or a young man who managed to build a new and productive postwar career in organic chemistry.

Leuchs worked for *I.G. Farbenindustrie* at Elberfeld, a company highly influenced by the ideas of Richard Kuhn and his assistant Dietrich Jerchel. In addition to the work described above, *I.G. Farbenindustrie* was the site for nerve gas research (11), and this association may have caused workers like Leuchs to make themselves unavailable after the war. However, it is possible to trace the incorporation of Leuchs's work into the corpus of postwar chemical knowledge recorded in English by examining the papers of Reid (12) and Ninehan (13) who cite many of Kuhn and Jerchel's papers (for example 14 and 15). Kuhn and Jerchel's work was also originally published in German and only became widely circulated in English after the war.

Acknowledgments

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About the Author

Michael Witty, Professor of Microbiology, Edison State College, 8099 College Parkway, Fort Myers, Florida 33919, is an empirical scientist with work published in ecology, botany, microbiology, molecular biology, biotechnology, history, zoology, and scientific education. He has lived or worked on every continent except Antarctica, though he is still young and ambitious.

THE KAMLET LABORATORIES COLLECTION AT THE UNIVERSITY OF SOUTH FLORIDA

Dean F. Martin and Karina Bidani, Department of Chemistry, University of South Florida, dfmartin@usf.edu

Introduction

Jonas Kamlet (1914-1960) and his wife Edna (1915-2011) founded the Kamlet Laboratory (as it was then called) in 1941 (1). It was in many ways a pioneering consulting laboratory that was unique for its approach and creativity. In 2006, the collected papers of the Kamlet Laboratories that were housed in two storage units in Sarasota, Florida, were donated to the University of South Florida (USF) Library, Tampa Campus, as noted elsewhere (1). This paper describes the background of the laboratory and indicates the potential value of the material in the Kamlet Chemical Laboratories Collection. The collection came to USF associated with a donation from Mrs. Edna Yadven Kamlet Rogers to establish the Jonas Kamlet Memorial Fund, which will help support preservation of the Collection (2). An online guide is available to provide a general view of collection (3).

We have given a few examples of the information available in the Collection, including some detail on one question, namely what was the financial picture in the early years? This paper describes the results of our examination of an account book that lists the income and expenses of the consulting laboratory for most of the first decade of its operation.

The Kamlets

The background of the Kamlets was considered previously (1), and some pertinent aspects are reviewed here. They had known each other for most of their lives, they came from similar backgrounds and their training complimented each other's. Jonas and Edna met when they went to their parents' summer cottages when they were nine years old. He came over to her, and said, "My name is Jonas Kamlet and I'm going to be a chemist." His family had come from Poland, hers from Russia (4).

Both were educated in New York City. He attended City College of New York, where he majored in chemistry and minored in biology and was graduated at the age of 16 during the early stage of the Great Depression. Edna Yadven majored in biology and minored in chemistry and was graduated from City University of New York (1,4). After college, he was employed in the laboratories of Israel Zion Hospital. Here he prepared derivatives of sulfa drugs (recently developed antibiotics) that he reported were 70 to 200 times more active than the parent compounds (5).

After starting the laboratory and becoming successful, Jonas Kamlet would be embarrassed when visitors would address him as "Doctor Kamlet," presumably impressed by his abilities. His wife told him to enroll in graduate school, promising that she would "mind the shop" (4). Subsequently, he entered graduate school and received his Ph.D. from New York University in 1944 (6).

Dr. Kamlet died in the prime of life at about 10:30 a.m. on Friday, December 16, 1960. He was returning

from a visit to Chicago as a passenger aboard a United Air Lines DC-8 jet that collided with a Trans World Airlines piston-engine Super Constellation over Staten Island. All 128 persons on the two planes and six on the ground died. Details and general background information are available elsewhere (7,8).

Dr. Kamlet's widow sued United Airlines (6), and her judgment was upheld by the New York Supreme Court. She received an award of $600,000 plus $45,000 interest. Though United Airlines was the defendant, "the Government agreed to pay $144,000 of the settlement because the Federal Aviation Agency had been issuing instructions to the planes at the time of the crash." At the time, the amount was "the largest settlement ever made as a result of an individual death," according to a newspaper account (9).

Mrs. Edna Yadven Kamlet (1915-2011) remarried in 1968 (Mr. Emil Rogers) and changed her name to Edna Rogers. After her second husband died, she moved to Sarasota in the late 1980s. There she became well known as a philanthropist. A library and the Opera House are named in Dr. Kamlet's honor (10). She was an enthusiastic supporter of the Sarasota opera and would buy tickets for the opening performance, as well as for a performance toward the end of the run because she noted differences between the two (4).

The Laboratories

The Kamlet Laboratory was founded in 1940 when the couple was married. The laboratory personnel consisted of Jonas and Edna Yadven Kamlet (4) with additional assistance hired on a consulting basis. The original laboratory was located at 250 East 43rd Street, New York, NY (1). At the time of Dr. Kamlet's death, the facility was called "the Kamlet Laboratories" and was located at 300 Fourth Avenue (surely a more impressive neighborhood). A second laboratory was created at 52 Sheridan Street, Stratford, Connecticut, near their home in Easton (4, 10). The specific addresses were copied from the Kamlet Papers (Figure 1).

The Kamlets' specialty was two-fold: consulting and/or developing inventions and selling the patent rights to interested companies. Mrs. Rogers spoke of having other employees to do analyses or development work, but dividing that work so that only she and her husband were aware of how the components would fit until the desired product was completed and patented (4). In any given year, the Laboratory would serve as a consultant to over 18 firms, based on a sampling of assigned patents (3).

Jonas Kamlet was ahead of his time, and highly creative, and Edna was certainly helpful (4). For example, among his many patents and inventions was a tablet that could be used to measure glucose in urine (1). He had commented to her that he needed a means of stirring, and she, thinking of Alka-Seltzer, suggested he should contact Miles Laboratories (Elkhart, Indiana) for persons experienced in providing agitation in water by chemical means. He presented the idea to Walter Compton, M.D., Medical Director at Miles Laboratories, who (Mrs. Rogers said) didn't know what to do with the idea/potential product (4). Ultimately, a patent was obtained by Miles Laboratories using attorneys in Chicago. The Kamlets earned $45,000 from the patent in five years; they had expected to earn $17 million (4).

Two additional points need to be made about this anecdote. First, Jonas Kamlet was able to make contact with a decision maker at a major firm; now such a person would probably be insulated by two layers of administrators. Second, he continued to consult for Miles Laboratories in a mutually beneficial way. As noted elsewhere (1) he helped to develop a process for recovering from paper-mill wastes what until then had been a costly substance used in the manufacture of Vitamin B_2. Working for Miles Laboratories, he ultimately obtained ten patents, all assigned to Miles, according to SciFinder Scholar.

Without question, Mrs. Kamlet's loss was a severe one, but she continued the activities of the firm for about twenty years until her retirement in her mid-sixties (10). We believe that the premature death of Dr. Kamlet was also a severe loss to the profession. It is difficult to assess what further inventions he and his wife might have formulated. Judging from the successful inventions up to the time of his death—a diabetes analysis pill, a pregnancy strip test, use of newsprint for animal feed, a fodder supplement, and many more, it is safe to conclude that many more impressive inventions might have been produced in the next two decades (1).

Representative Data from the Collection

The Collection is organized into eight finding aids (3). Those possibly of most interest to chemists include 1, personal materials of the Kamlet family; 2, personal materials of Jonas and Edna Kamlet; 3, copies of correspondence from the Laboratories to clients; 7, folders that focus on the patenting process for Jonas

Kamlet and his clients; and 8, scrapbooks of the Kamlets (Edna, Jonas, and his brother Mortimer).

Two examples may give a hint of the interesting material available to those engaged in historical chemistry.

First, the correspondence with Miles Laboratories from 1940-1945 shows the background of ten patents developed and assigned to Miles. Dr. Kamlet developed an effervescent tablet that could be used by physicians and others to measure the concentration of glucose in blood and urine, which led to a popular product called "Clinitest." The correspondence gives revealing insight into how he helped promote Clinitest by suggesting and offering assistance with an article to be written by a third-party author for a pertinent journal, through visits to firms he consulted for, through details given to Miles employees detailing the preparation of Clinitest, and by serving as a go-between with possible firms seeking a licensed use.

Second, pertinent data on the Kamlets' income and expenses are found in an account book (Figure 1) maintained at the Laboratory (11) and listed under the heading of "Personal Income." Entries began for May 1941 and continued through March 1945. The even (left-hand) pages have column headings of Months, Total Income, Household, and Laboratory. The adjacent odd pages have headings of Total Expense, Deficit, Surplus, and To Date. A curious entry on odd pages was Girls

with a single entry of $75.00 for September 1941, and the heading was no longer used after September 1945. Another interesting entry, labeled Pa, started in May 1941 with a last entry in January 1944. The amounts listed for Pa started with $200 for the first four months with the last five months listed as $44.00, and a range of values in between, with a low of $19.26 (September 1941) to a high of $224.18 (January 1942). The item was an expense item.
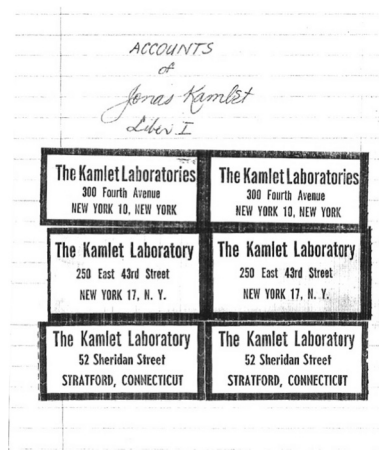

Figure 1. Picture of cover of the Liber I account book with laboratory return address labels.

For May 1941 (the first entry), the following data are available: Total income, $750.00; Household, $430.00; Pa, $200.00; Laboratory, $233.44. The sum of the last three values subtracted from the first gave a deficit of

Table 1. Financial development of Kamlet Laboratories, Year One (11)

Year	Month	Income, Total	Expense Laboratory	Total Expenses*	Deficit	Surplus	Value to date**
1941	May	$750.00	$233.44	$863.44	$113.44	---	$(113.44)
	Jun	750.00	218.61	861.46	111.46	---	(224.90)
	Jul	"	118.58	728.08	---	$21.92	(202.98)
	Aug	"	206.04	776.04	26.04	---	(229.02)
	Sep	818.75	278.32	768.28	---	50.47	(178.55)
	Oct	750.00	262.99	738.04	---	11.96	(166.59)
	Nov	"	224.03	792.27	42.27	---	(208.86)
	Dec	"	218.65	731.30	---	18.70	(190.16)
1942	Jan	743.39	268.37	833.30	89.91	---	(280.07)
	Feb	816.00	263.67	1085.60	269.60	---	(549.67)
	Mar	992.40	256.15	584.06	---	408.34	(141.33)
	Apr	1118.41	382.21	1082.99	---	35.42	(105.91)

* Total expenses include Household expenses (not listed separately here).
**( ) denotes a deficit.

Table 2. Financial development of Kamlet Laboratories, 1941-1955 (11)

Year	Month	Income, Total	Expenses, Laboratory	Total Expenses*	Deficit	Surplus	Value to date**
1941	May	$750.00	$233.44	$863.44	$113.44	---	$(113.44)
1942	Jan	743.39	268.37	833.30	89.91	---	(280.07)
	May	742.50	83.96	751.58	9.08	---	(114.99)
1943	Jan	707.60	20.82	513.05	---	$194.55	728.21
	May	715.10	84.88	771.21	56.11	---	1340.92
1944	Jan	1120.50	103.93	594.78	---	525.72	2339.04
	May	1250.00	387.22	936.29	---	313.71	2550.14
1945	Jan	2383.33	687.36	1473.01	---	910.32	7773.61
	May	2083.33	466.68	1103.68	---	979.65	11,592.06
1946	Jan	2083.34	707.49	2735.83	652.49	---	17,852.80
	May	2333.33	791.50	1611.00	---	722.33	20,709.22
1947	Jan	4083.37	799.66	5210.87	1127.50	---	32,546.13
	May	4083.33	1014.31	2219.31	---	1864.02	38,474.37
1948	Jan	3250.00	677.87	5733.06	2483.06	---	51,902.28
	May	4500.00	1066.48	2182.98	---	2317.02	56,792.97
1949	Jan	4250.00	773.32	2097.32	---	2152.68	72,615.00
	May	5361.84	1474.10	2334.45	---	3027.39	78,694.75
1950	Jan	5350.00	862.20	1924.90	---	3425.10	96,376.08
	May	5850.00	1786.31	2596.31	---	3253.69	103,571.07
1951	Jan	5850.00	1758.65	16,219.65	10,369.65	---	105,961.03
	May	5850.00	1495.52	2874.12	---	2975.88	113,002.36
1952	Jan	7350.00	2271.21	3641.80	---	3708.20	127,455.98
	May	6850.00	1677.71	2862.71	---	3987.29	138,230.30
1953	Jan	8500.00	4545.77	5723.16	---	2776.84	160,427.07
	May	7000.00	2200.17	3671.40	---	3328.60	164,628.43
1954	Jan	7000.00	2927.73	3960.34	---	4269.70	178,170.10
	May	7000.00	2498.17	3493.45	---	3506.55	201,476.93
1955	Jan	4500.00	1721.98	2646.98	---	1853.02	221,634.56

* Total expenses include Household expenses (not listed separately here).
**( ) denotes a deficit.

$113.44 for the first month of operation. Then in the first year of operation six months were deficits, six were labeled "Surplus" and the monthly results were calculated on an ongoing cumulative basis. As may be noted (Table 1), the cumulative deficit for the first year of operation was $105.91. (Note, however, that these figures reflect the Kamlets' overall finances, not just their business.)

The Kamlets became profitable fairly rapidly. (See Table 2 and Figure 2.) After the first year, up to January 1946 only four months out of 48 had a deficit. Generally, it seems that the months with a deficit were also months when there was an unusual increase in the Household entry, and sometimes this could be notable.

How successful was the laboratory? There seem to be two answers: On an absolute basis the results do not seem impressive, e.g., as of May 1949 (after seven years of operations) the cumulative surplus was $78,694.75. But bear in mind that $63 in 1949 would correspond to
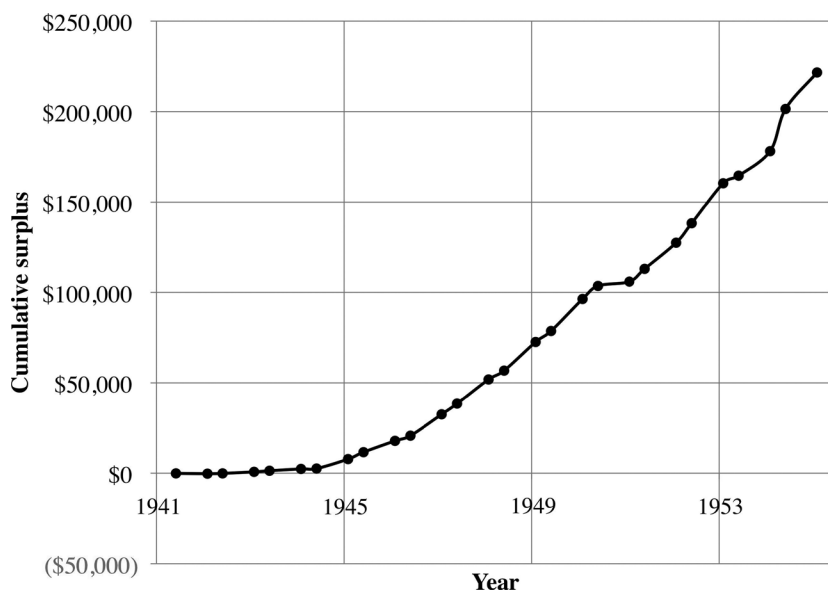
Figure 2. Net accumulated value in dollars over time, May 1941 (start) to January 1955.

$600 in 2011 dollars, according to a recent estimate, which would translate to a cumulative value of $747,000. In addition, the Kamlets were investing in Treasury bonds, stocks, and had a good bank account. In 1952 they earned stock dividends of $7,865.00 (equivalent to about $75,000). And in 1954, they sold their Connecticut home and netted $18,115.26 (i.e., about $172,000).

Finally, the papers could shed light on a range of other areas. One is how patent applications were developed, applied for, and defended; all are important topics. For example, the National Academy of Inventors,[TM] founded at USF in 2010, is concerned with showing the importance of patents in considering criteria for pay, promotion, and tenure in academe. Dr. Kamlet was a capable synthetic chemist, and may have been an early developer of one-pot sequential syntheses of organic compounds; his letters are informative. Correspondence for 1943, for example, with a single firm, was concerned with coumarin as an anticoagulant, recovering chemical value from the mycelial mat of *A. niger,* cation-exchange resin to remove iron from molasses in citric acid fermentation, effervescent colloidal aluminum hydroxide tablets for persons with ulcers, and a citric acid substitute (when there was a controlled supply for the war effort). In addition, correspondence covered *p*-thiocyanoaniline for its possible sulfanilamide-like activity, effervescent halazone tablets (for mouthwash, antiseptic, general germicide), an alternate synthesis of citric acid, pH Clinitest tablets, licensing arrangements for a Brazilian firm for "our tartaric acid process," and

a nasal vasoconstrictor (with information about patent application). The range of chemical products developed by the small firm in the mid-twentieth century was remarkable—from the clinical products already mentioned to fertilizer (in part from old newspapers). More personal matters might deal with sociological data about immigrants from eastern Europe, or the sacrifice Edna Kamlet made in giving up her artistic endeavors as a sculptor.

We can only imagine what the dual partnership of Jonas and Edna Kamlet might have achieved had it not been cut short.

Acknowledgments

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About the Authors

Dean F. Martin, Distinguished University Professor of Chemistry Emeritus, continues to be an active researcher. Karina Bidani, a high school senior, served as research intern in 2011.

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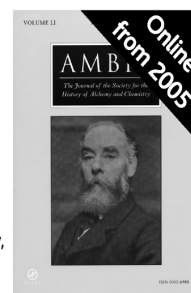**Dr Noel G Coley**, 24 Kayemoor Road, Sutton,
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BOOK REVIEWS

100+ Years of Plastics: Leo Baekeland and Beyond, E. Thomas Strom and Seth C. Rasmussen, Eds., Washington, DC: American Chemical Society, distributed in print by Oxford University Press, 2011, 193 pp, ISBN 978-0-8412-2677-7, $150.

Did humanity enter a new materials age in the 20th century? Have the archaeological eras known as the Stone, Copper, Bronze and Iron ages been supplanted by a new material? Did we enter a new "Plastics Age"?

E. Thomas Strom, Adjunct Professor at the University of Texas at Arlington, and Seth C. Rasmussen, Associate Professor of chemistry at North Dakota State University, use these questions as a starting point for their edited collection of chapters from the American Chemical Society's symposium "100+ Years of Plastics: Leo Baekeland and Beyond." While scholars have explored these specific questions before—in fact I do the same in a 2008 book on the history of polymer education and what I called the emergence of the "Polymer Age" (1)—it is one well worth asking again. These previous ages were defined by natural materials, and historian Brooke Hindle even called pre-Civil War America the "Wooden Age" (2). What is noteworthy about the 20th century is that it was the first material age that did not only come from nature, but instead was fundamentally a synthetic polymer.

This sets the stage for the significance of what Leo H. Baekeland (1863-1944) and others achieved through their work in plastics. It also forms the thematic cohesion behind the articles in Strom and Rasmussen's book, which is the published account of the papers presented on March 22, 2010, at the 239th ACS National Meeting in San Francisco, marking 100 years since the formation of the General Bakelite Company. Baekeland, as is familiar to many, made a name for himself and his product, Bakelite, by creating the first synthetic polymer that did not have a natural counterpart in 1907. Bakelite quickly found commercial success as an insulator for electric connections, and soon a host of other products emerged from telephones to teething rings. Fame quickly followed as *Time* magazine put Baekeland on its cover in 1924, and christened him as the "father of plastics" in 1939. The magazine has a long memory, and in 1999 its editors included him in their list of 100 most influential people of the 20th century.

This type of commercial and popular fame certainly deserves a symposium and book dedicated to his significance. Of the eleven articles in Strom and Rasmussen's book, the first four focus specifically on Baekeland and Bakelite. In a bit of an unusual approach in a scholarly tome, the first two of these are from family members. Carl B. Kauffman, who is related by marriage to the family, brings his experience in what is remarkably the only biographical treatment of Baekeland, which was his M.A. thesis from the University of Delaware. Hugh Karraker, Baekeland's great-grandson, writes the second chapter. The final two articles on the "father of plastics" come from Gary D. Patterson who discusses the details of Bakelite chemistry, and Burkhard E. Wagner who explores the evolution of the manufacturing of the product.

As a historian I wanted the rest of the book to have focused on Baekeland, his products, and its cultural significance but this was not the case. From this point on, the book does feel more like a haphazard, though important, presentation of symposium talks which all fall under the impossibly broad topic of "100+ years of plastics." The editors themselves admit this thematic divergence and rationalize it by saying that "Leo Baekeland's invention brought forth a flowering of polymer products, so the remaining chapters are much more diverse" (p. x). Les H. Sperling's article explores improvements in interpenetrating networks, while James Economy and Zeba Parkar contribute two co-written articles in which they examine resoles, novolaks, and related chemicals. James G. Traynham conveys the story of two of the "plastics pioneers" (Irvin I. Rubin and John L. Hull) in fabrication techniques with research coming from the oral history archive at the Chemical Heritage Foundation. Mehmet Demirors then tackles the history of what many consider the most widely used polymer—polyethylene. Co-editor Rasmussen follows with an examination of conducting polymers polypyrrole and polyaniline. As if there were not enough aspects of plastics history to explore in the 20th century, Wen-Bin Zhang, Stephen Z. D. Cheng, and Mike J. Yaszemski take the analysis into the 21st century with a history of musculoskeletal regenerative and reconstructive medicine.

Indeed, as the editors suggest, this is a "selective rather than a comprehensive survey of polymer history" (p. x). While chemists will enjoy learning more about these diverse topics, historians should demand more analysis on the genesis of the plastics age itself and its cultural ramifications (3). And that is a good thing, because this is a specialization in the history of chemistry that clearly needs more attention. Perhaps the real issue is: if the argument can be made that the 20th century gave birth to the "Age of Plastics," and if Leo Baekeland is the so-called "father of plastics" without a published biography, then there is a scholarly lacuna the size of a material epoch that needs to be filled.

Mark D. Bowles, Professor of History, American Military University, mdbowles@gmail.com

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Neither Physics nor Chemistry: A History of Quantum Chemistry, Kostas Gavroglu and Ana Simões, MIT Press, Cambridge, MA, and London, 2012, xiv + 351 pp, ISBN 978-0-262-01618-6, $40.

Neither Physics nor Chemistry is a multifaceted history of an "in between" discipline written by two of its foremost historians. The authors set out the parameters of their study in the brief introduction. They describe the development of the discipline from its origins through roughly 1970. Along the way, they concern themselves with six "clusters of issues." The first cluster has to do with "the historical becoming of the epistemic aspects of quantum chemistry" or what might be called the knowledge content of quantum chemistry and the foundations of that knowledge. The second is about the accretion of the trappings of a recognized

academic discipline such as conferences, textbooks, and chairs. Third is the "contingent character" of the development of quantum chemistry, the assertion that it could have taken different form had its developers had different research agendas, personalities, relationships, or modes of reasoning. Next is the reconsideration of the discipline's practices and goals that accompanied its adoption of digital computing. The fifth cluster is philosophical in nature, involving questions of reductionism, visualizability, and the roles of theory, rules, and mathematics. The final cluster is about "styles of reasoning" in quantum chemistry.

These clusters of issues certainly inform the narrative, but they do not structure it. Instead, the structure is mainly disciplinary, roughly geographical, and partly chronological. That is, the titles of the four chapters that contain the book's main narrative

explicitly refer to disciplines that contributed to quantum chemistry. Each chapter also has a geographic focus that is not explicit in its title. The first chapter, on quantum chemistry *qua* physics treats mainly developments in continental Europe. Chapter two, on quantum chemistry *qua* chemistry, is populated mainly by Americans. The third chapter, treating quantum chemistry *qua* applied mathematics, has a British focus. The fourth chapter is geographically cosmopolitan; it is also more disciplinarily diverse, beginning with researchers interested in biomolecules before it settles into the theme of its title, quantum chemistry *qua* programming. Within each of these chapters, the narrative is largely chronological, and the four chapters themselves form a slightly overlapping chronological sequence.

These four chapters of the book's main historical study are followed by a concluding chapter of historiographical considerations, largely reflecting on the role and nature of theory in chemistry. Notes, a bibliography, and an index occupy the final pages of the book. The bibliography of primary sources in quantum chemistry and historical works about it is extensive and impressive.

In the first chapter, the authors treat the application of quantum concepts to questions of chemical interest by the physicists who developed the old quantum theory and later quantum mechanics. They treat the first successful application of quantum mechanics to the chemical problem of binding, the 1927 paper by Walter Heitler and Fritz London in some detail. Not long afterwards, Paul Dirac would formulate both the promise and challenge of quantum chemistry from the perspective of many physicists: "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." In other words, Dirac asserted that chemistry is in principle reduced to quantum mechanics and that to solve problems of chemical interest requires finding mathematically tractable approximations within the framework of quantum mechanics.

In chapter two, one finds many American chemists and physicists whose names and concepts still appear in chemistry textbooks. Gilbert Lewis's model of bonding, involving shared electron pairs and octets, is described as arising out of pedagogical considerations. Linus Pauling is a key actor as both a developer of and advocate for the valence bond approach to quantum chemistry and the concept of resonance. Robert Mulliken's work on molecular spectroscopy and on the united-atom

limit of diatomic molecules are shown to inform his molecular orbital approach. John Slater, John Van Vleck, and George Wheland are also important figures in this chapter. The authors describe the connections among these figures, noting that American chemists and physicists communicated with each other, and so both chemists and physicists tackled problems of chemical interest. They contrast this situation with that in Europe, where physicists generally had little interest in chemical problems and chemists little mathematical training.

In chapter three, Charles Coulson emerges as a central figure, one who advocated a methodological diversity in quantum chemistry. His 1952 book *Valence* presented both the valence bond and molecular orbital approaches as useful within their ranges of applicability and asserted that trusting either alone would be foolish. (Slater and Van Vleck had written earlier on the complementarity of these two approaches and the mathematical equivalence of refinements to them.) John Lennard-Jones, who held the first chair of theoretical chemistry in the world (at Cambridge) and Douglas Hartree, of self-consistent field fame, are other principals in this chapter.

Chapter four begins in France, where quantum chemistry had been retarded by a long-standing aversion to theoretical science. The discipline "caught on" in inauspicious times—during and immediately after the German occupation of World War II. Investigations of the relationship between molecular structure and carcinogenesis gave French quantum chemistry a large-molecule biological flavor, and led to the "invention" of quantum biochemistry by Alberte and Bernard Pullman. Much of the rest of the chapter deals with the changes digital computers began to bring into quantum chemistry. The qualifier "digital" is needed in this context because in the earliest days of quantum chemistry, computers were people, not machines. The new computing machines gave quantum chemists the ability to increase the size of molecules they could treat or the accuracy of numerical calculations on small systems. The debate between advocates of *ab initio* and semi-empirical approaches, which had long been somewhat dormant because of the intractability of *ab initio* treatments for all but the smallest problems, re-emerged. During this time quantum chemistry became more of a mainstream part of chemistry, offering insights to practitioners of its more traditional subdisciplines. It also became more international, as exemplified by Masao Kotani's organizing international meetings in Japan and by Per-Olov Löwdin's *International Journal of Quantum Chemistry*.

The final chapter is on historiographical considerations of the emergence of quantum chemistry. It has a great deal of material relevant to the philosophy of chemistry, particularly on the role of theory in chemistry, the character of chemical theory, and the independence of chemistry from physics. Much of this chapter (and the end of the previous one) seems to me to belie the book's title, *Neither Physics nor Chemistry*. Rather it is consistent with the notion that quantum chemistry is a kind of chemistry with (at least some of) the character of chemistry and in service to the discipline of chemistry. At least that is where quantum chemistry landed, even though it clearly did not emerge entirely from within chemistry and it was certainly not shaped exclusively by chemists.

I am not a researcher in the history of this field, but I am familiar with the content of quantum mechanics and quantum chemistry and with the outlines of their history. It did not take long for me to come across historical facts I had not known. For example, quantization was applied to molecules before atoms: Niels Bjerrum formulated a treatment of vibrational and rotational spectroscopy that quantized rotation and assumed, semi-classically, that the frequency of the electromagnetic radiation matched the frequency of the motion. Fritz London was trained as a philosopher before he turned to physics. Unlike the philosophical writings of many early researchers in quantum mechanics, which were mainly popular accounts of the philosophical implications of their physical work, London's philosophical writings preceded his work in physics and were written for an audience of scholars in philosophy. Hans Hellmann, like many better-known scientists working in the 1930s, was caught up in the political upheavals that plagued Europe at the time: he left Nazi Germany for the Soviet Union, where he was executed in 1938 in Stalin's purges.

To praise the book primarily for such historical tidbits, however interesting, would be to trivialize its scholarship. One of its real strengths is the attention devoted to divisions or tensions of all sorts within the "in between" discipline of quantum chemistry. These include binary choices of valence bond vs. molecular orbital (personified by Pauling vs. Mulliken), quantitative vs. qualitative, visualizable vs. non-visualizable, and *ab initio* vs. semiempirical, as well as multipolar tensions among physics, chemistry, mathematics, biology, and computation, and among continental (German), American, British, and international approaches. One might even identify a tension between the either/or approaches of methodological partisans and the both/and approaches of pluralists.

I must, however, close with a caveat about the book's treatment of the technical content of quantum chemistry. Readers interested in details of methods like Hückel theory, self-consistent field calculations, or Slater-type orbitals, and in their development will be disappointed. To be fair, the stated theme of the book is the development of the subdiscipline of quantum chemistry, not the development of technical specifics within it. At the same time, the treatment of technical details when they do arise is not always done well. For example, the exposition of the Heitler-London paper states that only one of the two wavefunctions developed for the hydrogen atom is consistent with the Pauli exclusion principle. Heitler and London actually note that both hydrogen wavefunctions they consider are consistent with the Pauli principle, one with two different spins and the other with two identical spins; the former is the one that represents the bound molecule because that is the one that has an energy lower than isolated hydrogen atoms.

More often than not, technical details are absent, and rightly so for the purposes of the authors. What is present is a thoughtful, careful, and extensive study of the development of quantum chemistry from a strongly historical perspective informed by sociological and philosophical sensibilities.

Carmen J. Giunta, Professor of Chemistry, Le Moyne College, giunta@lemoyne.edu

African American Women Chemists, Jeannette Brown, Oxford University Press, New York, 2012, vii + 252 pp, ISBN 978-0-19-974288-2, $35.

Jeannette E. Brown's new book, titled *African American Women Chemists* is a wonderful gem. For the past several years, I have researched the biographies of several African American chemists as a passionate hobby, essentially becoming a *chemist-historian* by accident. I didn't specifically focus on African American women, but African American contributions to the field of chemistry in general. As a graduate student, it was almost therapeutic for me to learn about their stories. Thus, when Brown's book was published, I was absolutely thrilled. And I was more thrilled to write this review. Brown's book is a gem because it is the first book that solely focuses on the life, struggles and scientific achievements of African American women chemists. Divided into ten chapters, this book provides the reader with the personal journeys of 26 chemists, including Brown herself.

Why are these women significant? The 26 chemists that Brown profiles in this book focused on a variety of research topics such as the chemistry of Grignard reagents, the underlying causes of heart attacks and the development of photographic coatings. These women are significant because of their scientific contributions. Brown highlights that some of them were strong researchers and published their scientific contributions in high-impact journals, such as the *Journal of the American Chemical Society*, *Science, Journal of Biological Chemistry*, and the *Journal of Chemical Physics*. Quite simply, they are chemists that just so happen *to be* African American women.

Although this book is about the contributions of African American women chemists, it is a must read for everyone—not just African Americans. More importantly, this book is an easy read and is not targeted exclusively to the chemistry audience. Thus, *African American Women Chemists* could be used as a textbook for high school or college level courses in the fields of American history, history of science or within the chemistry curriculum.

Why is this book so important? In Chapter 1 ("The Reason for This Book and Why These Women Were Chosen") Brown writes, "Many people have studied the history of African American women chemists, but the information is scattered in many references, articles, and trade books. Until now, there was no one place where one could access extensive information about these women" (p 1). Thus, Brown indeed fills a "literary void" with

this important piece of work. In Chapter 2 ("Resources for Historical Background"), Brown provides a general overview of the topic and resources about African Americans in science, including *Beyond Small Numbers: Voices of African American PhD Chemists*, authored by Dr. Willie Pearson, and *Black Women Scientists in the United States*, by Dr. Wini Warren. But Brown clearly points out that most of the resources available about African American scientists focus on men, not women.

Brown also briefly describes what motivated her to write this book in the first place (p. 6):

> I began this study of the lives of African American women chemists after meeting Dr. Marie Daly at a scientific meeting in 1984. Dr. Marie Daly is the first African American woman to receive a PhD in chemistry. She was very modest and unassuming. Since I am also a chemist, I decided to learn about the other African American women who decided to pursue a degree in chemistry in spite of the odds against them.

Brown is actually emphasizing the importance and impact of role models, but she misses a great opportunity to discuss the topic. Specifically, what is needed is more detail on her meeting with Daly, which we can assume had a profound impact on Brown. What did Brown and Daly actually discuss? Career paths or the struggles Daly encountered in the field of chemistry? Was Daly a role model to Brown or a mentor? This is unclear.

One theme that truly resonates throughout this book is the importance of effective mentoring. Many women described in this book were mentored by both Black and White male chemists, which is not at all that surprising considering the smaller number of women chemists that could serve as role models. For example, Dr. Henry Ransom Cecil McBay and Dr. Kimuel Alonzo Huggins, both African American, mentored two chemists discussed in Brown's book, namely Dr. Gloria Long Anderson and Dr. Betty Wright Harris. Huggins and McBay both earned doctorates in chemistry from the University of Chicago, and published several articles in the *Journal of the American Chemical Society*. Moreover, McBay is considered to be the "Father of Black Chemists in the United States," because he mentored and trained several African American chemists during his academic career.

There have been numerous articles and books published about the low numbers of African Americans pursuing degrees in the chemical sciences and quite often a primary reason for these dismal statistics is the lack of effective mentoring. Due to the small numbers of

African American chemistry faculty, it is not statistically possible for every African American student interested in chemistry to be mentored by an African American faculty member. Brown's book clearly makes this point. To be an effective mentor or advisor, it is crucial that the mentor believes that the student can reach his or her full potential in the chemical sciences and provides solid training in both technical and soft skills.

In Chapters 3 ("Early Pioneers") through 8 ("Chemical Engineers"), Brown provides the reader with biographical information focused on the early life, education and career paths of each chemist. Although some detail regarding the early life for a few of the chemists in is quite limited, Brown does a very good job of emphasizing why each woman profiled is significant to the chemical sciences. Chapter 4 *("Marie Maynard Daly")* is an excellent and strong chapter focusing on the life of Daly, who earned her PhD under the guidance of Dr. Mary L. Caldwell, a pioneer for women chemists and expert in enzyme chemistry.

In Chapter 9 ("My Story"), Brown essentially tells of her own personal journey. A native of Bronx, NY, Brown knew at the age of five or six that she wanted to be a scientist. After earning a B.S. degree from Hunter College in 1956 and a M.S. degree in chemistry from the University of Minnesota in 1958—the first African American woman to earn a degree in chemistry from the University of Minnesota—Brown had a successful career in the pharmaceutical industry working for both CIBA Pharmaceuticals (now Novartis) and later Schering Plough (now Merck). Brown's research efforts focused on the development of pharmaceutical drugs including Primaxin, an antibiotic.

In Chapter 10 ("Next Steps"), the final chapter of the book, Brown discusses the importance of encouraging young women to major in chemistry and discusses in detail many resources available to help young people reach their full potential in the chemical sciences. The American Chemical Society (ACS) offers various programs such as Project SEED for high school seniors and the ACS Scholars Program which provides scholarships to underrepresented minority students. Additional ACS resources include the Women Chemists Committee (WCC) and the Committee for Minority Affairs (CMA). Brown also discusses the programming available through NOBCChE (The National Organization for the Professional Advancement of Black Chemists and Chemical Engineers) such its Science Bowl and Science Fair.

In this final chapter, Brown does a good job highlighting resources available; however, Chapter 10 could have been a stronger, more effective chapter if a brief discussion on effective mentoring were included. Obviously, there are academic institutions that have been successful producing African American women chemists with graduate degrees. But why are these institutions successful? What are common departmental factors among academic institutions for success? For women that are interested in academic careers, Brown briefly discusses wonderful opportunities available through COACh (Committee on the Advancement of Women Chemists). But, there are some African American women chemists that are successful tenured faculty. Why were these women successful at obtaining tenure? Honestly, in order to earn a graduate degree in the chemical sciences, one has to want the degree on a very personal level. But in order to increase the numbers of African American women with successful careers in the chemical sciences, these women quite simply need effective mentoring.

Sibrina N. Collins, Assistant Professor of Chemistry, The College of Wooster, scollins@wooster.edu.

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