

Word Count (main text): 8746

Word Count (main text w/ footnotes): 9981

Word Count (main text w/ notes & refs): 11498

Calibrating Chromatography: How Tswett Broke the Experimenters' Regress

Jonathan Livengood
University of Illinois at Urbana-Champaign

Adam Edwards
University of Illinois at Urbana-Champaign

Abstract. We propose a new account of calibration according to which calibrating a technique shows that the technique does what it is supposed to do. To motivate our account, we examine an early 20th century debate about chlorophyll chemistry and Mikhail Tswett's use of chromatographic adsorption analysis to study it. We argue that Tswett's experiments established that his technique was reliable in the special case of chlorophyll without relying on either a theory or a standard calibration experiment. We suggest that Tswett broke the Experimenters' Regress by appealing to material facts in the common ground for chemists at the time.

Keywords: Tswett, Experimenters' Regress, calibration, material theory

Acknowledgements: Thanks to John Norton, conference participants at the 2019 Midwest Junto for the History of Science, and three anonymous referees for helpful feedback on earlier drafts and presentations of this paper.

Calibrating Chromatography: How Tswett Broke the Experimenters' Regress

In this paper, we propose a new account of calibration according to which calibrating a technique (or instrument) is to show that the technique (or instrument) does what it is supposed to do. In other words, calibration establishes that a technique (or instrument) works as intended. To motivate our account of calibration, we examine an early 20th century debate between Mikhail Tswett (1872-1919) and Leon Marchlewski (1869-1946) about chlorophyll chemistry and the appropriate methods for investigating it. Tswett was a botanist whose interest in chlorophyll led him to develop chromatographic adsorption analysis (hereafter, CAA), a separation technique in physical chemistry.¹ Marchlewski was a prominent chlorophyll chemist who was highly critical of Tswett and his chromatographic method. In this paper, we focus on experiments that Tswett conducted to address Marchlewski's concern that the process of CAA altered the chemical character of chlorophyll. We argue that Tswett's experiments established that CAA was reliable in the special case of chlorophyll without relying on either a theory of CAA or a standard calibration experiment, which would have involved applying CAA to a mixture of known character (a surrogate signal) and verifying that CAA yielded the correct analysis. We then offer a guess as to Tswett's reasoning. We suggest that Tswett relied on material facts in the common ground for chemists at the time. By appealing to local material facts accepted by chemists at the time, Tswett answered his critic's complaint that his appeals to CAA were viciously circular and broke the Experimenters' Regress. We further suggest that Tswett did not conduct a standard calibration experiment because the

¹ Chromatography is usually defined as a physical separation technique in which a sample (the analyte) is distributed between a stationary phase (solid or liquid) and a mobile phase (liquid or gas). Separation occurs because the parts of the sample are differentially adsorbed.

material assumptions required to secure the reliability of CAA by way of a standard calibration experiment would have seemed dubious to chemists at the time.

Tswett developed CAA in 1902-1903. In subsequent years, he published several papers in which he used CAA to study the chemistry of chlorophyll, but the wider scientific community did not accept his technique as reliable until the 1930s. Livengood (2009) reviews a dozen explanations suggested in earlier literature for the initial rejection of Tswett's chromatography. He argues that chromatography was premature in the sense that it could not be properly connected with either entrenched chemical and botanical theories or entrenched laboratory practices.² In defending his *generalized prematurity* explanation of the rejection of chromatography, Livengood considers an alternative explanation that he attributes to Clark Glymour and Balázs Gyenis. According to Livengood (2009, 66-67), Glymour and Gyenis suggested in conversation that chromatography was initially rejected because Tswett did not carry out a calibration experiment showing that CAA produced similar results to entrenched techniques on samples of known character. Hereafter, we will use the label *s-calibration* to denote an experiment of the sort suggested by Glymour and Gyenis: one in which a new technique (or instrument) is applied to a standard or surrogate signal so that the deliverances of the technique may be checked. Granting that Tswett did not carry out an s-calibration experiment, Livengood argues that Tswett *did* calibrate his technique in a way that better fit his problem.

² "Rejection" here is to be interpreted loosely, since it is unlikely that most of the relevant scientists passed a negative judgment against chromatography so much as that they didn't know about it or simply ignored it.

The present paper expands on Livengood's story by connecting Tswett's development of chromatography with the Experimenters' Regress and the Material Theory of Induction.³ In Section 1, we discuss the problem of determining the number and properties of the parts of "raw chlorophyll" that occupied Tswett's attention in the last fifteen years of his life, and we describe the technique that Tswett developed in order to solve the problem as well as the experiments he performed in defense of his technique.⁴ In Section 2 we discuss the Experimenters' Regress and its relationship to challenges Tswett faced from two of his contemporaries: Willstätter and Marchlewski, and we argue that Tswett could not have broken the Regress by appealing to any "theory of the instrument" then available to him. In Section 3 we provide a detailed explanation of why Tswett did not carry out an s-calibration experiment. We argue that s-calibration would not have answered the only relevant objection to his technique *as applied to chlorophyll*. In the historical circumstances, it would have been unreasonable to assume that the character of chlorophyll was suitably similar to the character of any surrogate sample. Hence, s-calibration would not have addressed the worry that adsorption analysis somehow altered the character of the chlorophyll and so would not have broken the Experimenters' Regress. We then show how Tswett in fact broke the Regress by way

³ See Collins (1985), Collins (1994), Culp (1995), Franklin (1994), and Radder (1992) for early work on the Experimenters' Regress. See Norton (2003), Norton (2011), and Norton (forthcoming) for details on the Material Theory of Induction.

⁴ We use the expression "raw chlorophyll" to denote the mixture of pigments that gives leaves their color. Botanists and chemists today reserve "chlorophyll" for the green parts of what we call raw chlorophyll. Tswett acknowledges this distinction in his 1903 paper, writing, "It is well known that the term chlorophyll refers, and should refer exclusively, to the complex group of pigments, soluble in alcohol, to which vegetation owes its specific coloring" (8). For Tswett, "chlorophyll" is composed of (at least) five pigments, two of which are the "chlorophylls (chlorophyll α and β)." Tswett (1907b, 137) remarks again on the terminological problem, writing, "With justification or not, the supposed 'green component' of chlorophyll (also inexplicably referred to as chlorophyll) is generally regarded as the physiologically most important coloring material of the leaves."

of experiments he *did* perform. In Section 4 we argue that Tswett's case gives us reason to want a broader account of calibration. On a narrow account according to which calibration just is s-calibration, it seems that either calibration could not have served its epistemic function in Tswett's case or CAA simply could not have been calibrated with respect to chlorophyll. Accepting that we ought to give a broader account, we suggest looking to the epistemic function of calibration for theoretical guidance. We then propose an account of calibration according to which a calibration experiment is any experiment designed to show that an instrument does what it is supposed to do.

Section 1: The Explanatory Problem: Tswett and Chromatography

For most of his professional life, Tswett was concerned with the chemistry of chlorophyll and its role in photosynthesis. The problems of chlorophyll chemistry were well-established. In 1864, George Stokes sent a very brief communication to the Royal Society, which included some "remarks on the Constitution of Chlorophyll." In his note, Stokes says that he has been working for some time on the optical and chemical properties of chlorophyll. He writes, "I find the chlorophyll of land-plants to be a mixture of four substances, two green and two yellow, all possessing highly distinctive optical properties." As the nineteenth century ended, botanists and botanically-minded chemists knew that raw chlorophyll was a mixture of several distinct chemical compounds. However, no one knew the exact number of compounds, the proportions in which they occurred, their individual chemical structures and properties, and whether the answers to

these questions were different for different kinds of plant.⁵ Tswett (1906d, 388) emphasized the application of CAA to the problem of determining the number of the parts of raw chlorophyll, writing: “The green pigment of leaves, chlorophyll, is recognized as a pigment mixture of varying complexity as attacked by different investigators. Chromatographic analysis is qualified to finally determine the degree of this complexity.”⁶ Other chlorophyll researchers of the period, including Richard Willstätter (1872-1942), the winner of the 1915 Nobel Prize in Chemistry “for his researches on plant pigments, especially chlorophyll,” used a physical separation technique called *fractional partitioning*. But fractional partitioning is a difficult process, requiring large amounts of time, effort, and analyzable material. By 1902, Tswett was on the lookout for an alternative method and (perhaps) owing to his botanical training he found one.

Tswett had argued in his doctoral dissertation that chlorophyll was bound to plant leaves by adsorption. In 1902, he experimented with some 150 different adsorbent materials in an effort to formulate a general law of adsorption, which would further his understanding of the binding process in plants.⁷ He never discovered any law of adsorption, but his research led him to discover a simple and powerful physical separation technique that he immediately applied to the problems of chlorophyll chemistry, confirming “in a new, original way the view of Stokes” (Willstätter, 1915,

⁵ See Peirce (1903, 51-58) for a prospective look at the problems of chlorophyll chemistry. See Stewart (1918, 189-208) and Willstätter (1915) for retrospectives.

⁶ Throughout this paper, we provide English translations of the original German texts for the convenience of the reader, but owing to space constraints, we cannot include the original texts.

⁷ We don’t know *exactly* what Tswett’s experiments involved, since the details were never published and no laboratory record survives.

334) and making a large number of observations about the optical properties of the parts of raw chlorophyll.

In 1903, Tswett published his first description of his new technique of CAA.⁸ The method was elegant. One simply filled a slender glass tube with finely ground chalk or sugar, dissolved the substance being analyzed in a suitable solvent (for chlorophyll, this was calcium disulphide or petroleum ether), and poured the results into the tube. The different parts of the substance would be adsorbed at different rates by the same adsorbent, and so, the parts would separate out in bands along the adsorbing column. Since chlorophyll is a pigment, the separated parts would appear as distinct bands of color. Following separation, Tswett would push the chalk or sugar column out of the tube and cut the bands apart with a scalpel. He would then redissolve each part (itself a compound) in its own solvent and perform a spectral analysis.

To our minds, Tswett faced two substantive concerns about his application of CAA to chlorophyll and one methodological objection to his technique independent of its specific application. We will discuss in subsequent sections the methodological objection that Tswett's results were only supported by viciously circular appeal to his own method. In the rest of this section, we discuss the substantive concerns: namely, (1) that the sample might be chemically altered by interaction with the adsorbing material in the column and (2) that the sample might be oxidized during adsorption. As we will see in Section 2, Tswett's response to the substantive concerns underpins a response to the methodological objection as well. The first substantive concern was explicitly

⁸ An English translation of Tswett's 1903 paper was published with commentary in Hesse and Weil (1954).

acknowledged by Tswett, and he conducted experiments to directly address it.⁹ The second was raised by Willstätter and as far as we know Tswett was unaware of it.¹⁰ The two concerns are instances of a more general worry that the sample might be altered in some systematic way during adsorption. Tswett worried that the sample might be altered by chemical interaction with the adsorbent material. Willstätter worried that it might be altered in virtue of being adsorbed but not necessarily through chemical interaction with the adsorbent material.¹¹

As we argue in the rest of this section, Tswett's experiments sufficed to address both his own concern that there might be chemical interaction between the sample and the adsorbing column and also Willstätter's concern that the sample might be oxidized while in a more vulnerable adsorbed state. In fact, Tswett's experiments sufficed to address the general concern that the sample was altered in some systematic way during the adsorption analysis. Moreover, we argue that s-calibration would not have sufficiently addressed either of the substantive concerns.

In order to rule out the possibility of chemical interaction between the sample and the adsorbent column, Tswett (1907, 141-142) carried out three experiments. In his first experiment, Tswett conducted two simultaneous adsorption analyses using different adsorbent columns. He seems to have assumed that if the sample *had* chemically interacted with one or both of the adsorbents, then the pattern in subsequent spectral

⁹ Preliminary experiments with various solvents, adsorbates, and adsorbents are discussed in the 1903 paper and the experiments on chlorophyll specifically are presented in Tswett (1907b).

¹⁰ See Willstätter (1913, 147-149) for a short summary of an allomerization process that concerned him and Willstätter (1913, 237-242) for his concern about oxidation.

¹¹ Hence, we think that Livengood (2009, 66) is wrong when he says that Tswett's "only living doubt" was also expressed by Willstätter. Granted, Tswett's doubt and Willstätter's doubt are instances of a more general worry about chemical alteration of the sample during adsorption. However, the two specific concerns are not identical.

analyses would be different. However, the results of the spectral analyses were identical.

He writes (1907b, 141):

Although the adsorption on CaCO_3 makes the assumption of a chemical modification of the chlorophyll dyes very unlikely, and the spectra just identified are to be considered as ordinary dyes, I considered it necessary, for these results, to control these methods as far as possible by other methods. First, CaCO_3 was replaced by sucrose in the capillary water-tube, on the surface of which are OH^- ions. The results remained the same.

So, Tswett concluded that the sample was *not* chemically altered by the adsorbent. Taken as a general rule, Tswett's inference is unsound, since it is not always the case that different causes have different effects. However, the chemical facts in Tswett's specific case justify the inference in the way that Norton (2003, 2011, 2014, forthcoming) takes material facts to justify inductive inferences. Calcium carbonate (CaCO_3) and sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) have very different chemical properties so that it would be unlikely for them to have *identical* chemical interactions with a sample.

Tswett's first experiment makes it unlikely that the sample was altered by chemical interaction with the adsorbent column. By contrast, s-calibration would not have addressed Tswett's concern. An s-calibration experiment would assure users of CAA that samples suitably similar to the surrogate sample could be reliably analyzed with the method. But in the historical circumstances, the character of chlorophyll could not reasonably have been assumed to be suitably similar to the character of *any* surrogate sample. Looking back at the progress in chlorophyll chemistry, Willstätter (1918, 323) writes:

Some years ago, chlorophyll was unknown as a substance in a chemical respect. It was doubtful whether there was one chlorophyll or several pigments related to each other, or a great number of green leaf dyestuffs. The first questions of the analysis were unsolved; it was yet undecided which elements belonged to the chlorophyll molecule.

As such, an s-calibration experiment would not have provided much assurance that samples of chlorophyll—possibly very different from any test sample—would be separated by adsorption without chemically interacting with the column.

Tswett's first experiment made it *unlikely* that the sample was altered by chemical interaction with the adsorbent column. However, it was not definitive. Moreover, Tswett's first experiment didn't address Willstätter's concern that the sample might have been oxidized while in its adsorbed state. Happily, Tswett conducted two further experiments (probably because he recognized that the first experiment still left some room for doubt) that *did* serve to address Willstätter's concern. In his second and third experiments, Tswett began by conducting a spectral analysis of raw chlorophyll dissolved in alcoholic petroleum ether and then performing CAA to separate its parts. In the second experiment, he used fresh alcoholic petroleum ether to remove all of the adsorbed chlorophyll from the column and conducted a second spectral analysis. In the third experiment, he removed each separated part of the raw chlorophyll in its own alcoholic petroleum ether and then restored the raw chlorophyll in solution by mixing. Tswett concluded both experiments with another spectral analysis. In both experiments, he observed the same spectral absorption bands before and after the adsorption analysis. He writes (1907b, 141-142):

I further prepared chromatograms of chlorophyll on CaCO_3 and extracted them without decomposing them in alcoholic petroleum ether (with the addition of filtered carotene). The solution showed the same absorption spectrum as the initial adsorption used. In other experiments, the spectrum of the original solution was prepared by mixing the isolated, spectrally-analyzed dyes. Finally, chlorophyllin α , even without adsorption, was presented in small quantities: with emery and CaCO_3 , crushed *Taxus* leaves were thoroughly extracted with pure petroleum ether to remove the carotene as much as possible. The pulp was then extracted by means of alcoholic petroleum ether and shaken with 80% alcohol to remove the

xanthophylls and the chlorophyllin β , the latter being more soluble in said alcohol than chlorophyllin α . Then the petroleum ether solution was shaken with stronger (90%) alcohol, which absorbs most of the chlorophyllin, while the petroleum ether solution mainly retained the last traces of carotene. The chlorophyllin, dissolved in petroleum ether, then showed the already known spectrum, especially the weak bands IV and V, in the same position and intensity.

Tswett does not say explicitly, but he seems to have assumed that if two samples produce the same absorption bands, then they are very likely to be samples of the same substance. If so, his second and third experiments provided strong evidence that his samples were not being altered by chemical interaction with the adsorbent columns. Tswett's experiments *also* provided strong evidence that the sample was not being altered in any other way. If the sample were altered by oxidation as Willstätter suggested, then the absorption bands in the initial spectral analysis would be different from the absorption bands in the final spectral analysis. Since the entire adsorption process is bracketed by the spectral analyses, any alteration is detectable. The specific source of the alteration makes no difference to the power of the experiment to detect it.

At the beginning of this section, we said that Tswett faced two substantive concerns and one methodological objection. We have explained how Tswett's experiments answered the substantive concerns that the sample might be altered in some way during the adsorption process and why s-calibration would not have answered those concerns. In the next section, we turn to the methodological objection.

Section 2: Marchlewski's Challenge and the Experimenters' Regress

Beginning in 1906, Tswett carried on an extensive and bitter published exchange with Leon Marchlewski, a prominent chemist of the period, regarding CAA and its application to chlorophyll. Livengood (2009, 64) distills four distinct lines of objection in

Marchlewski's part of the exchange: (1) that Tswett's experimental results differed from the results obtained using entrenched techniques of partition and crystallization; (2) that the conclusions Tswett drew from his experimental results disagreed with entrenched theories of chlorophyll; (3) that CAA "did not sufficiently resemble accepted analytical practice"; and (4) that Tswett's arguments for his new technique were viciously circular. For our purposes, the third objection may be set aside. The first two objections make the fourth pressing. If Tswett's results *had* agreed with results obtained from entrenched techniques and implications of entrenched theories, that agreement would have supported the claim that CAA was reliable. As Livengood (2009, 66) observes, the results reported in Willstätter's 1913 book should have served as a post hoc calibration of CAA, since Willstätter's analysis "confirm[ed] Tswett's results in all essentials." But at the time of Tswett and Marchlewski's exchange, the disagreement between their results required resolution. One had to decide which results to endorse. Of course, one need not have rejected the existing *techniques* in order to endorse Tswett's results. If the conflicting results from existing techniques were due to improper use, then one could still endorse Tswett's results without threatening the general reliability of the existing techniques. Marchlewski (1907b, 226-227) complained that endorsing the results from CAA would require independent evidence that the results from the entrenched techniques were incorrect.

But Mr. TSWETT not only sins in methodological terms, he uses apodictic statements that have no value in science. Our results must be wrong, simply because they disagree with his! Mr. TSWETT would first have to prove why the criteria we use are insufficient to assess the purity of the chlorophyll we are describing, and as long as he does not do so on the basis of exact experiments, I must leave any further remarks in relationship to Mr. TSWETT unanswered. (227)

Without independent evidence, relying solely on CAA to establish the reliability of CAA—as Marchlewski alleged that Tswett had done—would be viciously circular.

The difficulty that Marchlewski raised has a similar underlying logic to what Collins (1985) calls *the Experimenters' Regress* (see especially 83-89 and 100-103). Radder (1992, 67) argues that Collins describes—but does not explicitly distinguish—two different versions of the Experimenters' Regress: a vicious infinite regress and a vicious circle.¹² For our purposes, the vicious circle form of the Experimenters' Regress is more important, since it is the logic of the vicious circle form that underwrites Marchlewski's criticism of CAA.¹³ Hence, we focus on the vicious circle form and set aside the regress form. The vicious circle form amounts to the worry that (1) in order to know that an experimental apparatus, technique, or method is reliable, one needs to know that its deliverances are reliable but (2) in order to know that the deliverances are reliable, one needs to know that the apparatus, technique, or method is reliable.¹⁴ Marchlewski's challenge to CAA appears to have been exactly that Tswett could not have justification for both (1) and (2) with respect to CAA solely on the basis of CAA itself.

Before describing Tswett's response to Marchlewski in detail, we consider and reject an alternative way of trying to break the Experimenters' Regress by appealing to what is sometimes called a theory of the instrument. We argue that such a theory was

¹² Recent papers by Feest (2016) and Zuppone (2017) suggest that the two forms of the Experimenters' Regress are conflated in Collins but in fact have different targets, as well as different structures.

¹³ Zuppone (2017) argues that as a general rule, the regress form is subordinate to the vicious circle form (which she calls “general reciprocity”).

¹⁴ We think the vicious circle form of the Experimenters' Regress is essentially a version of a very general puzzle in epistemology that Chisholm (1982) calls *the problem of the criterion*. He writes (62), “To know whether things really are as they seem to be, we must have a *procedure* for distinguishing appearances that are true from appearances that are false. But to know whether our procedures [sic] is a good procedure, we have to know whether it really *succeeds* in distinguishing appearances that are true from appearances that are false. And we cannot know whether it does really succeed unless we already know which appearances are *true* and which ones are *false*. And so we are caught in a circle.”

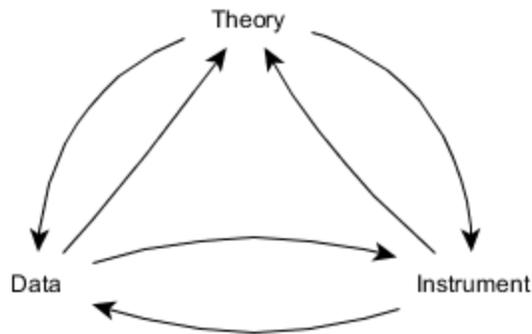
unavailable to Tswett. The fact that no theory of the instrument was available to Tswett made Marchlewski's objection—essentially the vicious circle form of the Experimenters' Regress—pressing. It also makes what Tswett ultimately did that much more impressive.

As we've seen, Marchlewski demanded that Tswett provide independent reason to think that the results of the entrenched techniques were incorrect because he thought that CAA could not undermine the entrenched results on its own without vicious circularity. The justificatory picture that Marchlewski assumed looks like this:



The arrows in the diagram represent a justification relation. The reliability of the instrument (in this case, CAA) justifies the reliability of the data, and the reliability of the data justifies the reliability of the instrument. Put more simply, a good instrument produces good data, and good data are produced by a good instrument. Hence, Marchlewski's challenge shares its logical structure with the vicious circle form of the Experimenters' Regress.

In discussing the Experimenters' Regress, Collins supposes both that the only rational justification for claiming that an instrument is good is that it produces good data and also that the only rational justification for saying that some data are good is that they are produced by a good instrument. But this is an impoverished view of experimentation. Scientists typically have access to more than just the data and the instruments that produce the data. At the very least, the picture has to be complicated as follows:



In this picture, “theories” may be understood either widely or narrowly. Understood narrowly, a theory is an explicit account of the behavior of an instrument that typically warrants belief in the reliability of the instrument. Such a theory may be called a *theory of the instrument*. For example, optical theory provides an account of the behavior of the microscope and warrants belief in its reliability. Understood widely, theories include broad assumptions about the objects of study, experimental design, or instrumentation more generally. A theory in the wide sense may even include epistemic and metaphysical assumptions about the scientific method, laws of nature, causation, and so on.

There are cases where no narrow theory exists—that is, cases where there is no explicit theory of the instrument. In such cases it is tempting to think that a genuine data-instrument circle must arise and that the Experimenters’ Regress is a serious problem. Chromatography appears to be just such a case. Adsorption was not well understood during Tswett’s lifetime. Tswett appealed to theoretical work by Gibbs in order to justify the claim that the parts separated by adsorption analysis were optically and chemically distinct. However, Gibbs’ theoretical work was not well-suited to answering Marchlewski’s challenge given what was known about adsorption at the time.

In an important paper “On the Equilibrium of Heterogeneous Systems,” Gibbs

(1878) derived an equation relating the concentration of a substance adsorbed on a surface and the surface tension at the boundary. Gibbs' equation is as follows:

$$d\sigma = -\eta_s dt - \Gamma_1 d\mu_1 - \dots - \Gamma_n d\mu_n$$

When the system is at equilibrium, entropy (represented here by η_s) goes to zero and the density of the substance(s) $\Gamma_1 \dots \Gamma_n$ adsorbed at the boundary between the adsorbent and the adsorbate is equal to the ratio of the surface tension at the boundary and the chemical potential of the adsorbate ($d\sigma/d\mu_i$). Gibbs' equation idealizes ordinary systems by assuming a homogeneous distribution of adsorbate across a geometric surface. Tswett (1908) cited Gibbs' work as translated in Ostwald's 1892 volume, *Thermodynamische Studien*.¹⁵ In a footnote Tswett explains how Gibbs' equation connects chemical potential and adsorption. Tswett writes:

Adsorption, as first discussed by GIBBS (Thermodynamic Studies, p. 271), is based on the pursuit of minimum surface energy at the boundary between a solid and a liquid. If a solute reduces the surface energy, it accumulates at the boundary and is adsorbed. If, therefore, we have several solutes, as in a petroleum-chlorophyll solution which passes through a column of powder, we first adsorb the one which most strongly reduces the surface energy, and only then, i.e. below, the next active substance is recorded; and we get as many different zones as there are various dissimilar surface energy-reducing substances in solution.

Clearly CAA was not entirely without theoretical foundation. But could Gibbs' work have provided a theoretical background from which Tswett could answer Marchlewski's challenge and escape the Experimenters' Regress? We think not.

First, Gibbs' derivation was controversial during Tswett's lifetime, and the theory of adsorption remained unsettled for a long time afterward. For example, Lewis (1908 and 1909) carried out numerous empirical tests of the Gibbs equation and found that in

¹⁵ Livengood (2009) mentions this footnote, but identifies the wrong 1908 article.

many cases, the “actually determined values for Γ far exceeded the calculated values” (1909, 467). We find the following observation in a very detailed review of the literature on adsorption written nearly a decade after Tswett’s death:

Many attempts have been made to obtain confirmation of the equation, but the great experimental difficulties have prevented any definite conclusion being reached. Donnan has recently said “the question whether the simplified form of the Gibbs equation yields a sufficiently accurate value for the excess surface concentration can scarcely be decided without further experimental evidence.”¹⁶

Hence, an appeal to Gibbs’ work would not have been convincing. Tswett could, perhaps, have appealed to Freundlich’s (1907) empirically-derived adsorption equation or to Milner’s (1907) theoretical proof of Gibbs’ equation. But Tswett did not cite either of them and we have no reason to think that he was aware of their work. Langmuir’s (1918) theoretical adsorption equation came too late to be of any use to Tswett.

Second, a theory of adsorption is not equivalent to a theory of chromatography. Explicit theories of chromatography were not developed until significantly after the technique was rediscovered and applied by Lederer, Kuhn, and others in the 1930s. Having a theory of chromatography requires (at least) having a theory of solute retention and a theory of solute dispersion. According to Cazes and Scott (2002, p.4), “There are two fundamental chromatography theories that deal with solute retention and solute dispersion and these are the *Plate Theory* and the *Rate Theory*, respectively.” Plate theory was introduced by Martin and Synge in 1941 and first put into the form typically used today by Said in 1956. Rate theory was introduced by Amundson in work published in the late 1940s and early 1950s on the mathematics of adsorption in beds. The upshot is that there was no theory of chromatography itself until long after Tswett’s introduction of

¹⁶ Swan and Urqhart (1926, p.256)

the technique.

Third, and most importantly, even if there had been an explicit theory of chromatography during Tswett's lifetime, such a theory would not have answered all of the concerns raised by Marchlewski and Willstätter about alteration of the sample. A theory of chromatography might allay *some* concerns, but it wouldn't address the most salient one: namely, that CAA altered *chlorophyll* in some way. Since an explicit theory of chromatography wouldn't have lessened the worry that CAA was altering the chlorophyll sample, Gibbs' much less detailed theory of adsorption wouldn't have done so either.

Section 3: Breaking the Regress: A Material Approach

In the absence of an explicit theory adequate to assure skeptics that the chlorophyll sample was unaltered by Tswett's technique, we think that it appeared to Marchlewski that CAA fell into a genuine data-instrument circle. But Marchlewski was mistaken. There were material facts outside the data-instrument circle available to Tswett. He could have appealed and we think *did* appeal to facts about spectroscopic analysis and chemical interaction in order to justify his claims about chlorophyll. In this section, we reconstruct the reasoning Tswett employed in more detail. We think our reconstruction is historically plausible, and we intend for it to be understood as a conjecture about how Tswett and Marchlewski reasoned about CAA and chlorophyll chemistry. However, neither Tswett nor Marchlewski is as explicit about his reasoning as we would like, and as far as we know, there are no surviving laboratory notes or letters that might give us insight beyond the published record. Our reconstruction is informed by the whole pattern of

argumentation in Tswett (1903, 1906a, 1906b, 1906c, 1906d, 1907a, 1907b, 1907c, 1907d, 1907e, 1908a, 1908b, 1908c, 1908d, 1908e, 1908f, 1908g, 1910, 1911a, 1911b, and 1911c), Marchlewski (1902, 1906a, 1906b, 1907a, 1907b, 1907c, 1908a, 1908b, 1908c, 1908d, 1911), and Jacobson and Marchlewski (1912a and 1912b). But we have found it difficult to isolate short passages that clearly support each step that we take. We encourage curious and skeptical readers to look closely at Tswett and Marchlewski's papers, to raise specific challenges to our reconstruction, and to frame a plausible alternative.

In reconstructing Tswett's reasoning, we have been inspired by Norton's material theory of induction (see Norton 2003, 2011, 2014, forthcoming), according to which there is no universally-applicable, purely formal rule of inductive inference and no global fact (such as the "fact" that nature is uniform) that warrants every inductive inference. Rather, each inductive inference is powered by a *local* matter of fact. We find that paying attention to local matters of fact throws substantial light on the debate between Tswett and Marchlewski. As we have already said, we intend our reconstruction to be read as a conjecture about what actually happened in a specific moment in the history of science. However, at least some interesting theoretical claims may be made on the basis of our account understood as a merely possible, rational reconstruction of the case. For example, we want to say that actual working scientists sometimes appeal to local matters of fact in order to break the Experimenters' Regress. To support that claim, we need a plausible account of what actually happened. But in order to support the weaker modal claim that scientists *could* break the Regress by appealing to local matters of fact (without a robust theory of an instrument and without conducting any s-calibration experiments), our

account merely needs to possible.

We take Tswett's central argument to be for the claim that all raw chlorophyll has the parts $\{C_1, C_2, \dots, C_N\}$ in the fixed proportions $\{P_1, P_2, \dots, P_N\}$.¹⁷ The argument proceeds from the character of a sample of chlorophyll as follows:

[A1] (tacit, background assumption) Samples of chlorophyll are exchangeable with respect to how many parts the sample has and the proportions in which those parts occur; that is, what is true of one sample is true of every sample.

[A2] This sample of chlorophyll has the parts $\{C_1, C_2, \dots, C_N\}$ in the proportions $\{P_1, P_2, \dots, P_N\}$.

===== (therefore inductively)

[A3] Every sample of chlorophyll has the parts $\{C_1, C_2, \dots, C_N\}$ in the proportions $\{P_1, P_2, \dots, P_N\}$.

[A1] is either a generalization for inductive inference or a universal claim in a deductive argument. Here we present it as the former. In either case, the evidence for [A1] is a material fact that is part of chemical theory in the wide sense: two samples of the same substance are exchangeable with respect to their chemical properties. This is a "material fact" in Norton's sense of the term. Tswett initially appealed to CAA in order to justify [A2], e.g. in his claim that "chromatographic analysis is qualified to finally determine the degree of [the] complexity [of chlorophyll]" (1906d, 388).¹⁸ The sub-argument for [A2] runs as follows:

[B1] CAA separates this sample of chlorophyll into the parts $\{C_1, C_2, \dots, C_N\}$ having proportions $\{P_1, P_2, \dots, P_N\}$.

[B2] If so, then this sample of chlorophyll has the parts $\{C_1, C_2, \dots, C_N\}$ in the proportions $\{P_1, P_2, \dots, P_N\}$.

¹⁷ Most of the exchange between Tswett and Marchlewski deals with chlorophyll in the strict sense, meaning Tswett's chlorophyll- α and chlorophyll- β . Tswett (1908c, 1352) claimed that the two chlorophylls occur in ether solution in the ratio 5:1. Citing that paper, Jacobson and Marchlewski (1912, 221) say that Tswett maintained the view "that the two are always present in the ratio of 1:5." Of course, Tswett recognized that the raw chlorophyll included xanthophylls and carotenes as well. So, the claim we are attributing to Tswett is an abstracted schema that we think he would have endorsed.

¹⁸ See also, Tswett (1906c, 322).

[A2] This sample of chlorophyll has the parts $\{C_1, C_2, \dots, C_N\}$ in the proportions $\{P_1, P_2, \dots, P_N\}$.

We present the sub-argument for [A2] as deductive, but one might construe it as a broadly inductive argument by weakening or qualifying the premisses as needed.

Marchlewski's version of the Experimenters' Regress challenged [B2] by emphasizing that Tswett did not know whether the sample was chemically altered during the adsorption process. We take the objection to have this form:¹⁹

[M1] If we don't know whether the sample was chemically altered during the process of CAA, then we should not endorse [B2].

[M2] We don't know whether the sample was chemically altered during the process of CAA.

[M3] We should not endorse [B2].

The claim that the sample was being altered during the adsorption process was a reasonable provisional hypothesis explaining the difference in results between the entrenched techniques and Tswett's new technique. A cautious approach would tend to favor the entrenched techniques and Marchlewski's explanation.

¹⁹ There are several ways one might characterize this argument. First, we may alter the target of Marchlewski's objection. On our view the target isn't CAA itself, but about whether Tswett is warranted to accept [B2] given what he knows about CAA. There may be reasons to prefer an objection that attacks B2 directly, although this appears more faithful to the objection Marchlewski actually leveled against Tswett. Second, we may alter the strength of the objection. On the one hand, we might interpret the objection as about the mere possibility of the sample's being altered. This interpretation would replace premise [M1] with, "If it is possible that the sample was chemically altered..." Such an objection seems far too demanding if one has in mind metaphysical or even physical possibility. On the other hand, we might interpret the objection as about only some "live hypotheses" relevant to alteration of the sample. In this case [M1] would focus on whether we've eliminated relevant alternative explanations for the results. This seems more plausible but is weaker than our reconstruction above.

Tswett responded by arguing directly for the disputed conditional [B2] and supporting his argument with experimental evidence that chlorophyll samples were unaltered by his application of the adsorption process. We think he reasoned as follows:²⁰

[C1] If CAA doesn't chemically alter the parts of chlorophyll during separation, then [B2].

[C2] CAA doesn't chemically alter the parts of chlorophyll during separation.

[B2] If CAA separates this sample of chlorophyll has the parts $\{C_1, C_2, \dots, C_N\}$ having proportions $\{P_1, P_2, \dots, P_N\}$, then this sample of chlorophyll has the parts $\{C_1, C_2, \dots, C_N\}$ in the proportions $\{P_1, P_2, \dots, P_N\}$.

Premiss [C1] is taken to be a part of the background chemical theory to which Tswett can appeal. That is, [C1] was among the material facts that were accepted by chemists and botanists at the time.²¹ After all, if CAA doesn't chemically alter the substances it is intended to separate, there is no reason to be suspicious of its results. Premiss [C2] is what Tswett sets out to support.²² How could he be sure that the chlorophyll wasn't being chemically altered during analysis? Tswett appealed to material facts about chemical interaction and spectral analysis. His first experiment yields the following argument:

[D1] CAA of chlorophyll using chalk as an adsorbent yields the same spectroscopic results as CAA of chlorophyll using sugar as an adsorbent.

[D2] If so, then CAA doesn't chemically alter the parts of chlorophyll during separation.

[C2] CAA doesn't chemically alter the parts of chlorophyll during separation.

²⁰ See especially Tswett (1906c, 319) and Tswett (1906d, 386).

²¹ Some version of [C1] is likely to be accepted by all experimentalists: if an experimental technique doesn't confound a result, then if the technique produces some result, then the result is the case.

²² See Tswett (1906a, 319) on chemical interactions between chlorophyll and various solvents and Tswett (1906b, 386) for interactions between chlorophyll and absorbents. And see especially, Tswett (1907b, 141), where he describes his calibration experiments.

Tswett's first experiment and the corresponding argument above are not entirely adequate. The argument effectively assuages the worry that the chlorophyll chemically interacts with the adsorbent, but it doesn't rule out the possibility that the chlorophyll is altered in some other way, e.g. by interacting with atmospheric oxygen while adsorbed, as Willstätter worried. Tswett's second and third experiments are more successful. We lay out the argument as follows:

[E1] A spectroscopic analysis conducted before CAA and a spectroscopic analysis conducted after CAA yield identical results.

[E2] If so, then CAA doesn't chemically alter the parts of chlorophyll during separation.

[C2] CAA doesn't chemically alter the parts of chlorophyll during separation.

Here, the experimental result is given in [E1], and [E2] depends on two background chemical facts: (1) no chemical alteration of the chlorophyll that occurred during the adsorption process would be reversed by re-dissolving the chlorophyll and (2) spectroscopic analysis would detect any chemical differences between the initial sample in solution and the final sample in solution. Again, these were background facts that botanists and chemists accepted.

Tswett's experiments *did not* show that CAA was reliable with respect to all mixtures whatsoever, but they achieved something quite remarkable nonetheless. Tswett provided a method for testing the reliability of CAA for each mixture to be analyzed. Given an unknown sample, one could repeat Tswett's experiments to check whether adsorption analysis altered samples of that type. Compare Tswett's achievement to s-calibration. The *hope* with s-calibration is to establish the general reliability of the calibrated technique by showing that it correctly separates a sample of known

composition. But it would have been good enough in Tswett's case if s-calibration could have been used to establish that CAA was reliable with respect to chlorophyll. One might offer the following argument:

[F1] CAA doesn't chemically alter the parts of a known test sample during separation.

[F2] If so, then CAA doesn't chemically alter the parts of chlorophyll during separation.

[C2] CAA doesn't chemically alter the parts of chlorophyll during separation.

The problem, though, is that for [F2] to be plausible, the test sample needs to be (relevantly) chemically similar to the target raw chlorophyll sample. If the test sample is chemically very different from raw chlorophyll, then the inference is precarious. In the case of a sample of essentially *unknown* character, the fact needed to secure [F2] is simply unavailable.

An anonymous referee wondered whether Tswett could have appealed to some *other* facts in order to make use of s-calibration to argue for [C2]. If so, then our claim that s-calibration could not have used s-calibration to show that CAA worked with respect to chlorophyll. We think this is unlikely. Consider the following plausible-looking approach. Although very little was known about raw chlorophyll, Tswett's contemporaries did know that raw chlorophyll is a mixture of very unstable organic pigments and that the entire mixture is insoluble in water but soluble in ether. Perhaps Tswett could have used another mixture of organic pigments as a surrogate and argued as follows:

[G1] CAA doesn't chemically alter the parts of this mixture of organic pigments during separation.

[G2] If so, then CAA doesn't chemically alter the parts of chlorophyll during

separation.

[C2] CAA doesn't chemically alter the parts of chlorophyll during separation.

However, in order to confirm [G1], Tswett would have needed to know the chemical character of at least one organic pigment (or better, pigment mixture) that could have been assumed to be not-too-different in relevant respects from the parts of chlorophyll. Some organic pigments were well-understood by the early 1900s. For example, Baeyer had described the structure of alizarin and indigo in the 1860s and 1870s.²³ However, the pigments with known structures were comparatively simple, much more stable, and unlike chlorophyll in some chemically important ways, such as being soluble in water but not in ether. Better surrogate organic pigments, such as carotin, hemoglobin, and lutein were not well-understood at the time. Carotin was investigated using CAA in the late 1910s by the American chemist Leory Palmer.²⁴ Hemoglobin, which has an extremely similar chemical structure to chlorophyll α , was being studied at around the same time as chlorophyll. Interestingly, Marchlewski, in collaboration with another Polish scientist, Marcell Nencki, had established the close chemical relation between chlorophyll and hemoglobin by showing that they had very similar decomposition products.²⁵ But the structure of hemoglobin was not determined until the x-ray crystallography work by Max Perutz et al. (1960), so it could not have been used as a surrogate. Similarly, the structure of lutein was not well-understood until the work of Richard Kuhn in the 1930s.²⁶ So, we think Tswett would not have found the G-argument congenial. Of course, this is only one

²³ See Nagendrappa (2014).

²⁴ See Ettre and Zlatkis (1979) for discussion of some (re)discoveries of chromatography after Tswett, and see Ettre and Wixom (1993c) for discussion of Palmer specifically.

²⁵ See Skarzynski (1946).

²⁶ See Orna (2013, 124-125).

possible route to securing [C2] by way of s-calibration. Perhaps there are other routes that would work better, but we do not know of any plausible ones. Hence, we maintain that s-calibration would not have served Tswett's aim or broken the Regress.

In this section we've suggested that Tswett had some material facts available to him that were powerful enough to justify his technique. Furthermore, the calibration experiments Tswett performed were sufficient to answer the objections Marchlewski raised and to break the Experimenter's Regress. However, these experiments do not meet the orthodox definition of calibration in Collins (1985), Franklin (1994, 1997), etc. In the next section we address calibration directly.

Section 4: Calibration

The orthodox view among philosophers, at least until recently, appears to be that calibration just is s-calibration. With some recent exceptions that we will discuss later in this section, every account of calibration we know of says that a calibration experiment for an instrument or method uses some input of known character to show that the instrument or method gives the correct output for some of the inputs in its scope. These experiments then support the claim that the instrument or method will likewise give the correct output for a novel input. Collins (1985, 105) writes: "Calibration is the use of a surrogate signal to standardize an instrument. The use of calibration depends on the assumption of near identity of effect between the surrogate signal and the unknown signal that is to be measured (detected) with the instrument." Franklin (1994) disputes Collins'

account of the measurement of gravity waves and presents an alternative version of events but does not dispute Collins' account of calibration.²⁷ Franklin (1997, 31) writes:

Calibration, the use of a surrogate signal to standardize an instrument, is an important strategy for the establishment of the validity of experimental results. If an apparatus reproduces known phenomena, then we legitimately strengthen our belief that the apparatus is working properly and that the experimental results produced with that apparatus are reliable.

Writing about the (alleged) use of intuitions as evidence in philosophy, Cummins (1998, 116-117) gives a similar account:

Every scientific subdiscipline spends a good deal of effort identifying and correcting errors and artifacts. What is important for present purposes is that an observational technique is deemed acceptable just to the extent that it can be relied upon to produce accurate representations or indicators of its targets. This is why observational procedures in general, and instruments in particular, have to be calibrated. When Galileo pointed his newly devised telescope at the moon and saw mountains—earthlike blemishes on what should have been a perfect celestial object—it was legitimate for the opposition to inquire whether the apparent mountains were artifacts. The proper response was to point the telescope at something of known size, shape, distance, color, and so on to determine what distortions it introduced; to calibrate it, in short.

And the orthodox view that calibration just is s-calibration seems to be the standard view among working scientists, as well.²⁸

Tswett's case gives us some reason to want a broader account of calibration: one that does not simply identify calibration with s-calibration. Tswett was able to break the Experimenters' Regress by relying on facts about chemical interaction and spectral analysis that were in the common ground for chemists of his time, not by appealing to a

²⁷ Whereas Collins argues that no calibration experiment can provide independent support for the adequacy of the surrogate signal (and hence, that calibration fails to provide an escape from the Regress), Franklin argues that physicists thought carefully about the adequacy of the surrogate signal and had good (experimental) reasons for thinking that it was a good surrogate.

²⁸ For evidence, consider the definition of "calibration" in the International Vocabulary of Metrology report by the International Bureau of Weights and Measures.

detailed theory of chromatography or by conducting an s-calibration experiment. We think it is plausible to regard Tswett's experiments as calibrating CAA. But as we've seen, Tswett's experiments do not involve a surrogate signal. He did not establish the reliability of CAA with respect to some samples of known character and then infer that the technique would also apply to chlorophyll. Rather, he conducted experiments that directly established the reliability of CAA *as applied to chlorophyll*. Here, then is a simple argument that some calibration experiments are not s-calibration experiments.

[H1] Tswett's experiments served to calibrate CAA.

[H2] If [H1], then either Tswett's experiments involved a surrogate signal or some calibration experiments are not s-calibration experiments.

[H3] Tswett's experiments did not involve a surrogate signal.

[H4] Some calibration experiments are not s-calibration experiments.

We think that [H2] and [H3] will be accepted by everyone. But one might worry that [H1] is question-begging. We think that [H1] is a naïve, pre-theoretical categorization judgment and as such is not question-begging with respect to any *theory* of calibration. However, we do acknowledge that [H1] is a rather thin support. Here, then, is an alternative argument that rests on rather different grounds:

[J1] If calibration just is s-calibration, then either Tswett could not have calibrated CAA with respect to chlorophyll or calibration of CAA with respect to chlorophyll could not have fulfilled any of its epistemic functions.

[J2] Tswett could have calibrated CAA with respect to chlorophyll.

[J3] If calibration just is s-calibration, then calibration of CAA with respect to chlorophyll could not have fulfilled any of its epistemic functions.

We think that it should always be possible to calibrate an instrument or technique in a way that fulfills the epistemic functions of calibration. But if so, then calibration is not just s-calibration.

A third argument motivated by our first two proceeds as follows. We have appealed to a categorization judgment in our first argument, but we expect that judgment to be controversial. Hence, we are motivated to find a more widely-acceptable way to constrain theories of calibration. Inspired by our second argument, we think that a plausible way to constrain theorizing about calibration is to focus on its epistemic functions. If one accepts that a good account of calibration should make sense of its epistemic functions, then one will be inclined to accept a broader account of calibration to the degree that a broader account does a better job making sense of the epistemic features of calibration.

At this point we want to highlight the ends that calibration serves according to Collins, Franklin, and Cummins in the passages we quoted earlier in this section. For Collins, calibration is primarily about standardization, which is very important for communication within and across laboratories. For Franklin, calibration is about establishing that an instrument is functioning properly and that experimental results are valid. For Cummins, it's about identifying and excluding artifacts and errors. Paying attention to the epistemic function of calibration suggests that surrogate signals are incidental to calibration. What matters is that an experiment promotes standardization, facilitates successful communication across research laboratories, establishes that an instrument is functioning properly, allows for the identification and exclusion of artifacts and errors, and generally ensures that an instrument is reliable. With our constraint in

mind, we propose to think of calibration in the following way: An experiment is a calibration experiment if it is designed to establish that an instrument or technique does what it is supposed to do.²⁹ We now develop our proposal by comparing it with accounts of calibration from the recent literature. Current discussion of calibration in philosophy appears somewhat sporadic. While we have not conducted any empirical studies of philosophers' views on calibration, we have found evidence that some philosophers of measurement endorse something like the orthodox view. For example, Soler and colleagues (2013) develop a framework for calibration in established contexts using standardized instruments. In such a context, calibration tests are of two kinds: blank tests, where a measurement is performed "in the absence of any object" of the relevant type in order to detect noise (e.g. the tare weight of a scale or allowing an empty balance to come to equilibrium), and "etalon" tests, where the instrument is applied to an etalon, which the authors use as a technical term for "a metrologically certified measurement standard or an object with sufficiently well-known and stable properties" (289) and the results are compared against the etalon's value.³⁰

An account that is much closer to the one we present comes from Perovic (2017, 317), who says that "*any combination of experimental techniques that ensures the proper functioning of the apparatus based on already-known phenomena* may be characterized as calibration." (emphasis in original) We agree that calibration is ultimately aimed at establishing that an instrument is functioning properly. As we read him, what separates

²⁹ An experiment is a *successful* calibration experiment if it actually establishes that an instrument or technique does what it is supposed to do. For those who want "calibrate" to be a success term, drop "design" from our account and make adjustments as necessary.

³⁰ The VIM the French translation of "calibration" is "étalonnage" meaning more directly something like the act of étalon-ing or "standardizing."

Perovic's account from ours is the phrase "already-known phenomena," which we take to require a comparison between the deliverances of an instrument to be calibrated and something independently known about the target of application for the instrument. For example, one might point a telescope at an object whose basic properties are already known by way of direct perception, as we saw Cummins suggest earlier, or one might point a microscope at a disc whose markings are already known because they are manufactured, as Hacking (1983, 203) argues. Hence, we read Perovic as offering an orthodox account.

Other recent accounts of calibration dispense with surrogate signals and measurement standards, defining calibration in terms of what they take to be characteristic aims, instead. For example, Tal (2017, 33) defines calibration as a process of identifying parameter values in a measurement model. He writes:

Calibration is a special kind of modelling activity where the system being modelled is a measurement process. The primary aim of calibration is to identify which parameter values in the model [of a measurement process] coherently and accurately predict the final states of the measurement process.

This account, Tal says, differs from several others "in its emphasis on coherence and predictive accuracy as the central aims of calibration, and in deemphasizing the epistemic role of measurement standards" (44). We agree with Tal that deemphasizing measurement standards and other surrogate signals is an important step in understanding calibration, but we think that by focusing on measurement his view does not correctly identify the characteristic aim of calibration in general: establishing that an instrument does what it is supposed to do.

Similarly, when discussing procedures for calibrating newly invented instruments, Soler (2015, 105) writes:

In practices dedicated to the invention of new instrumental devices, as in any other type of scientific practices, calibration minimally refers, at the most general level, to the achievement of a reliable instrument-token (typically a measurer) regarding some *mesuranda*.

Soler's account here is very close to ours. But there is a difference that turns on how one understands the phrase "reliable instrument-token." Since Soler is talking about reliability *regarding some mesuranda*, we understand an instrument-token to be reliable if it is highly likely that the instrument accurately represents the thing being measured.³¹ On our view, calibration establishes that an instrument does what it is supposed to do. We often want our instruments to deliver sufficiently accurate measurements with high probability. Consequently, in those cases our account says the same thing as Soler's. However, an instrument might do exactly what it's supposed to do without delivering accurate measurements with high probability. Let's illustrate the difference with some examples.

Consider a device that is supposed to produce a random integer in the range from 1 to 100. An experimenter uses this instrument when randomly sampling from a target population. And an experimenter might get evidence confirming or disconfirming the claim that for any number in the range, the probability that the device outputs that number is 1/100 (or at least close to it). To calibrate the device is not to show that it is accurately measuring anything. The numbers delivered by the instrument are not

³¹ Later in Soler's essay she discusses cases in which a new instrument is being actively developed. She refers to these as NewLI practices (for New Local Instruments). However, in such cases she says that calibration is a demonstration that "the instrumental outputs of the new instrument *cohere* with what is already taken for granted in the present stage of scientific development" (emphasis in original). As we've discussed above coherence with alternative separation techniques was unavailable to Tswett and would have only been another instance of s-calibration.

measurements. But the experimenter still wants to know that the device is doing what it is supposed to do. We might say that the experimenter wants to know that the instrument *reliably* produces a random number. But in saying this, we should not be understood as saying that the experimenter wants to know that with high probability, the device accurately represents something that is being measured. Rather, we should be understood as saying that with high probability the instrument does what it is supposed to do, i.e. generate a number in the range from 1 to 100 such that for any number in that range, the probability of that number being generated is 1/100.

The randomizer is a special case of a larger category of instruments that we might call *producers* or *generators*, which are calibrated by establishing that they generate what they are supposed to generate. For example, calibrating a laser might involve establishing that it outputs coherent light at a specific (intended) wavelength. Or suppose that an experimenter designs a device to “knock” a system out of equilibrium at regular intervals by impressing a specific (intended) force to an object in the system. As with the randomizer, we aren’t trying to establish that these devices are accurately measuring anything. The experimenter need not use these devices to measure anything in order to be interested in knowing that the instrument generates the output it is supposed to generate.

From Tswett’s work it is clear that what CAA is supposed to do is separate the component parts of chlorophyll without chemically altering them in any way. Tswett’s technique does not measure the parts of chlorophyll. That step comes later, when Tswett separates and weighs the bands produced in the adsorbent column or when he performs spectral analysis on the component parts to identify their chemical structure. The separation technique is supposed to separate the parts of chlorophyll effectively and

without alteration. The experiments that Tswett performed demonstrate that this is, in fact, what his technique does and it's for this reason that we consider them to be calibration experiments.

Section 5: Conclusion

Let's take stock. We have seen that recognizing the threat of the Experimenters' Regress has value in scientific inquiry insofar as it pushes investigators to show that their techniques work as advertised and to do so in ways that avoid falling into the Regress. The work Tswett performed to justify CAA in the face of objections by Willstätter and Marchlewski was valuable for this reason. However, we have seen no reason to think that the Regress is an unavoidable epistemic sink. The Experimenters' Regress is not the basis of a sound skeptical argument. Rather, we have seen how to break the Regress by appeal to background theoretical principles, often in the form of local material facts. We reflected on Tswett's example and what it can tell us about calibration more generally. And finally, we defended the view that an experiment is a calibration experiment if it establishes that an instrument or method does what it is supposed to do.

References

- Amundson, N. R. (1948). A Note on the Mathematics of Adsorption in Beds. *The Journal of Physical Chemistry*, 52(7), 1153-1157.
- Amundson, I. N. R. (1950). The Mathematics of Adsorption in Beds. *The Journal of Physical Chemistry*, 54(6), 812-820.
- Brühl, J. W. (1901). Roscoe-Schorlemmer's Lehrbuch der organischen Chemie. (E. Hjelt & O. Aschan, Eds.). Retrieved from <http://hdl.handle.net/2027/mdp.39015077330333>
- Cazes, J., & Scott, R. P. (2002). *Chromatography Theory*. New York: CRC Press.
- Collins, H. (1985). *Changing Order: Replication and Induction in Scientific Practice*. London: Sage Publications.
- Collins, H. (1994). "A Strong Confirmation of the Experimenters' Regress." *Studies in the History and Philosophy of Science* 25, 493-503.
- Culp, S. (1995). "Objectivity in Experimental Inquiry: Breaking Data-Technique Circles." *Philosophy of Science* 62, 438-458.
- Ettre, L. S., & Zlatkis, A. (Eds.). (1979). *75 Years of Chromatography: a Historical Dialogue*. Amsterdam: Elsevier Scientific Publishing Company.
- Ettre, L.S. (1980). "Evolution of Liquid Chromatography: A Historical Overview." In Horváth 1980, 1-74.
- Ettre, L.S. and K.I. Sakodinskii (1993a). "M.S. Tswett and the Discovery of Chromatography I: Early Work (1899-1903)." *Chromatographia*, 35, no. 3/4, 223-231.
- Ettre, L.S. and K.I. Sakodinskii (1993b). "M.S. Tswett and the Discovery of Chromatography II: Completion of the Development of Chromatography (1903-1910)." *Chromatographia*, 35, no. 5/6, 329-338.
- Ettre, L.S. and Wixom, R.L. (1993c). Leory Sheldon Palmer (1887-1944) and the beginnings of chromatography in the United States of America. *Chromatographia*, 37(11-12), 659-668.
- Franklin, A. (1994). "How to Avoid the Experimenter's Regress," *Studies in the History and Philosophy of Science* 25, 463-491.
- Franklin, A. (1997). Calibration. *Perspectives on Science*, 5(1), 31-80.

Freundlich, H. (1907). "Über die Adsorption in Lösungen," *Zeitschrift für Physikalische Chemie*, 57(1), 385-470.

Gibbs, J.W. (1878). "On the Equilibrium of Heterogeneous Substances," *American Journal of Science and Arts (1820 - 1879)* 16(96), 441-459.

Gibbs, J.W., & Ostwald, W. (1892). *Thermodynamische Studien*. Leipzig: W. Engelmann.

Hesse, G. and H. Weil (1954). *Michael Tswett's First Paper on Chromatography*. Germany: M Woelm Eschwege.

Horváth, C., ed. (1980). *High-Performance Liquid Chromatography, Volume 1: Advances and Perspectives*. New York: Academic Press.

Jacobson, C.A. and Marchlewski, L. (1912a). On the Duality of Chlorophyll and the Variable Ratio of the Two Constituents. *American Chemical Journal*, 47, 221-231.

Jacobson, C.A. and Marchlewski, L. (1912b). Methods for Determining Neo- and Allochlorophyll in the Presence of One Another. *American Chemical Journal*, 48, 111-124.

JCGM, J. (2012). 200:2012—International Vocabulary of Metrology—Basic and General Concepts and Associated Terms (VIM). Technical Report.

Langmuir, I. (1918). "The adsorption of gases on plane surfaces of glass, mica and platinum," *Journal of the American Chemical Society*, 40(9), 1361-1403.

Lapidus, L., & Amundson, N. R. (1952). Mathematics of adsorption in beds. VI. The effect of longitudinal diffusion in ion exchange and chromatographic columns. *The Journal of Physical Chemistry*, 56(8), 984-988.

Lewis, W. C. M. (1908). "An experimental examination of Gibbs's theory of surface-concentration, regarded as the basis of adsorption, with an application to the theory of dyeing." *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 15(88), 499-526.

Lewis, W. C. M. (1909). "An experimental investigation of Gibbs's theory of surface-concentration, regarded as the basis of adsorption. (Second Paper.)" *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 17(100), 466-494.

Livengood, J. (2009). "Why was M.S. Tswett's Chromatographic Adsorption Analysis Rejected." In *Studies in History and Philosophy of Science*, 40, 57-69.

- Marchlewski, L. (1902). Zur Chemie des Chlorophylls. *Journal für Praktische Chemie*, 65(1), 161–167.
- Marchlewski, L. (1906a). Über die chemischen Beziehungen zwischen Blatt- und Blutfarbstoff. *Berichte der Deutschen Botanischen Gesellschaft*, 24, 146-148.
- Marchlewski, L. (1906b). Zur Abwehr. *Berichte der Deutschen Botanischen Gesellschaft*, 24, 534–535.
- Marchlewski, L. (1907a). Studien über natürliche Farbstoffe. *Biochemische Zeitschrift*, 3, 287-306.
- Marchlewski, L. (1907b). Über Herrn Tswetts historische Chlorophyllforschungen und seine Chlorophylline. *Berichte der Deutschen Botanischen Gesellschaft*, 25, 225-228.
- Marchlewski, L. (1907c). Zur Chemie des Chlorophylls. *Biochemische Zeitschrift*, 5, 344-345.
- Marchlewski, L. (1908a). Zur Phylloxanthinfrage. *Biochemische Zeitschrift*, 7, 282–285.
- Marchlewski, L. (1908b). Studien in der Chlorophyllgruppe. *Berichte der Deutschen Chemischen Gesellschaft*, 41(1), 453–455.
- Marchlewski, L. (1908c). Studien in der Chlorophyllgruppe. *Biochemische Zeitschrift*, 10, 131-166.
- Marchlewski, L. (1908d). Bemerkungen zu Hrn. Tswetts Mitteilung: Über die nächsten Säurederivate der Chlorophylline. *Berichte der Deutschen Chemischen Gesellschaft*, 41(2), 1858–1860.
- Marchlewski, L. (1911). Über die Dualität der Chlorophyllane. *Biochemische Zeitschrift*, 3, 332-333.
- Martin, A. J. P., & Synge, R. M. (1941). A new form of chromatogram employing two liquid phases: A theory of chromatography. 2. Application to the micro-determination of the higher monoamino-acids in proteins. *Biochemical Journal*, 35(12), 1358.
- Milner, S. R. (1907). “On surface concentration, and the formation of liquid films,” *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 13(73), 96-110.
- Nagendrappa, G. (2014). Johann Friedrich Wilhelm Adolf von Baeyer. *Resonance*, 19(6), 489-522.
- Norton, J. (2003). A material theory of induction. *Philosophy of Science*, 70(4), 647-670.

- Norton, J. (2011). History of science and the material theory of induction. *European Journal for Philosophy of Science*, 1(1), 3-27.
- Norton, J. (2014). A material dissolution of the problem of induction. *Synthese*, 191(4), 671-690.
- Norton, J. (forthcoming). *The Material Theory of Induction*. Retrieved from: http://www.pitt.edu/~jdnorton/papers/material_theory/material_theory_June_26_2018_to_c.pdf
- Orna, M. (2013). *The Chemical History of Color*. New York: Springer.
- Peirce, G. J. (1903). *A Text-Book of Plant Physiology*. Henry Holt and Company: New York
- Perovic, S. (2017). Experimenter's regress argument, empiricism, and the calibration of the large hadron collider. *Synthese*, 194(2), 313-332.
- Radder, H. (1992). "Experimental Reproducibility and the Experimenters' Regress." *PSA: Proceedings of the Biennial Meeting of the Philosophy of Science Association*, Volume One: Contributed Papers, 63-73.
- Radder, H. ed. (2003). *The Philosophy of Scientific Experimentation*. Pittsburgh: University of Pittsburgh Press.
- Said, A. S. (1956). Theoretical-plate concept in chromatography. *AIChE Journal*, 2(4), 477-481.
- Schryver, S. B. (1909). The Chemistry of Chlorophyll. *Science Progress in the Twentieth Century*, 3(11), 425-449.
- Skarzynski, B. (1946). Professor Leon Marchlewski. *Nature*, 157(3994), 650-651.
- Soler, L. (2015) "Calibration in scientific practices which explore poorly understood phenomena or invent new instruments" in Schlaudt, O., & Huber, L. (Eds.). (2015). *Standardization in measurement: Philosophical, historical and sociological issues*. (pp. 95-110) Routledge.
- Soler, L., Wieber, F., Allamel-Raffin, C., Gangloff, J. L., Dufour, C., & Trizio, E. (2013). Calibration: A conceptual framework applied to scientific practices which investigate natural phenomena by means of standardized instruments. *Journal for General Philosophy of Science*, 44(2), 263-317.
- Stokes, G. G. (1864) On the supposed Identity of Biliverdin with Chlorophyll, with remarks on the Constitution of Chlorophyll. *Proceedings of the Royal Society*, 13, 144-145.

- Swan, E., and Urquhart, A. R. (1927). Adsorption equations. *The Journal of Physical Chemistry*, 31(2), 251-276.
- Tal, E. (2017). Calibration: Modelling the measurement process. *Studies in History and Philosophy of Science Part A*, 65–66, 33–45. <https://doi.org/10.1016/j.shpsa.2017.09.001>
- Tswett, M. (1903). On a New Category of Adsorption Phenomena and their Application to Biochemical Analysis. *Proceedings of the Warsaw Society of Natural Sciences, Biological Section*, 14. Reprinted in Hesse and Weil.
- Tswett, M. (1906a). Zur Ultramikroskopie. *Berichte der Deutschen Botanischen Gesellschaft*, 24, 234.
- Tswett, M. (1906b). Zur Kenntnis der Phaeophyceenfarbstoffe. *Berichte der Deutschen Botanischen Gesellschaft*, 24, 235-244.
- Tswett, M. (1906c). Physikalisch-chemische Studien über das Chlorophyll. Die Adsorptionen. *Berichte der Deutschen Botanischen Gesellschaft*, 24, 316–323.
- Tswett, M. (1906d). Adsorptionsanalyse und chromatographische Methode: Anwendung auf die Chemie des Chlorophylls. *Berichte der Deutschen Botanischen Gesellschaft*, 24, 384–393.
- Tswett, M. (1907a). Zur Geschichte der Chlorophyllforschung. Antwort an Herrn Marchlewski. *Berichte der Deutschen Botanischen Gesellschaft*, 24, 71-74.
- Tswett, M. (1907b). “Spektralanalytische Untersuchungen über die Chlorophylline und deren nächste Säurederivate (Chlorophyllane).” *Berichte der Deutschen Botanischen Gesellschaft*, 25, 137-149.
- Tswett, M. (1907c). Zur Chemie des Chlorophylls. Über Phylloxanthin, Phyllocyanin und die Chlorophyllane. *Biochemische Zeitschrift*, 5, 6-32.
- Tswett, M. (1907d). Über die Spektrophotometrie der Chlorophylline und die Energetik des Chlorophylls. *Berichte Der Deutschen Botanischen Gesellschaft*, 25, 388-397.
- Tswett, M. (1907e). Nochmals über das Phylloxanthin. *Biochemische Zeitschrift*, 6, 373-378.
- Tswett, M. (1908a). Über die Verfärbung und die Entleerung des absterbenden Laubes. *Berichte der Deutschen Botanischen Gesellschaft*, 26, 88-93.
- Tswett, M. (1908b). Über das Pigment des herbstlich vergilbten Laubes. *Berichte der Deutschen Botanischen Gesellschaft*, 26, 94-101.

Tswett, M. (1908c). Über die nächsten Säurederivate der Chlorophylline. *Berichte der Deutschen Chemischen Gesellschaft*, 41, 1352-1354.

Tswett, M. (1908d). "Ist der Phosphor an dem Aufbau der Chlorophylline beteiligt?" *Berichte der Deutschen Botanischen Gesellschaft*, 26, 214-220.

Tswett, M. (1908e). Über das Phaeophytin und die Chlorophyllane nebst Schlußbemerkungen über das Phylloxanthin. *Biochemische Zeitschrift*, 10, 404-413.

Tswett, M. (1908f). Über die Natur des sogenannten „krystallisierbaren Chlorophylls" (Metachlorophyllins). *Biochemische Zeitschrift*, 10, 414-425.

Tswett, M. (1908g). Das neue System der sogenannten Chlorophyllderivate. *Biochemische Zeitschrift*, 10, 426-429.

Tswett, M. (1910). Das sogenannte »krystallisierte Chlorophyll« — ein Gemisch. *Berichte der Deutschen Chemischen Gesellschaft*, 43(3), 3139-3141.

Tswett, M. (1911a). Über den makro- und mikrochemischen Nachweis des Carotins. *Berichte der Deutschen Botanischen Gesellschaft*, 29, 630-636.

Tswett, M. (1911b). Über Reicherts Fluoreszenz-Mikroskop und einigen damit angestellten Beobachtungen über Chlorophyll und Cyanophyll. *Berichte der Deutschen Botanischen Gesellschaft*, 29, 744-746.

Tswett, M. (1911c). Über die Löslichkeitsverhältnisse der Chlorophylline und eine neue Methode zur Isolierung derselben. *Berichte der Deutschen Chemischen Gesellschaft*, 44(1), 1124-1127.

Westreich, D. et.al. (2018) "Target Validity and the Hierarchy of Study Designs" *American Journal of Epidemiology*, 188(2), 438-443.

Zuppone, R. (2017). An Internal Answer to the Experimenters' Regress through the Analysis of the Semantics of Experimental Results and Their Representational Content. *Perspectives on Science*, 25(1), 95-123.