

The Marsh Test for Arsenic

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Historically the favorite and most famous of all poisons is arsenic, though the arsenic in question was generally not the pure chemical element itself but rather its oxide, As_2O_3 or diarsenic trioxide, otherwise known with equal inaccuracy as white arsenic. Indeed, since the most common form of this compound is actually composed of discrete As_4O_6 molecules, it should more properly be called tetraarsenic hexaoxide.

For centuries proof of arsenic poisoning was problematic at best. True chemical tests for its presence did not appear until the late 18th century and most of these relied on precipitation of the arsenic as a characteristic colored compound, such as yellow $\text{As}_2\text{S}_3(\text{s})$ or diarsenic trisulfide (Hahnemann's Test) (1). Unfortunately, when analyzing a sample of stomach fluid, for example, various other stomach contents were often coprecipitated with the arsenic leading to masking of the result and to a corresponding ambiguity in the evidence.

Origins of the Marsh Test

Such a problem was encountered in 1832 when a British chemist in the employ of the Royal Arsenal at Woolwich by the name of James Marsh (figure 1) was



Figure 1. James Marsh (1794-1846).

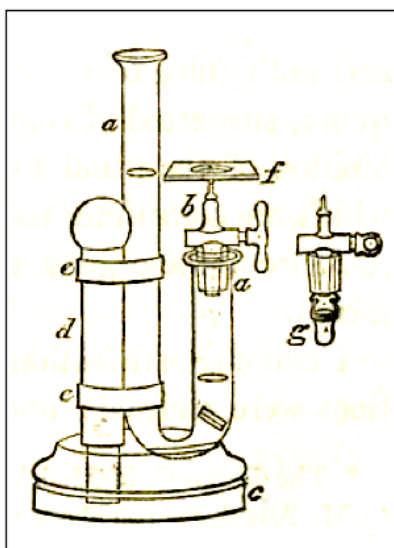


Figure 2. Marsh's original apparatus as depicted in his paper of 1836.

called upon to give expert testimony at the trial of one John Bodle, who was accused of poisoning his grandfather by putting arsenic in his coffee. Marsh successfully detected arsenic using Hahnemann's test but found that his precipitate deteriorated with time due to the gradual deposition of other material. As a result, the jury was unconvinced and Bodle was found innocent, though he later confessed to the crime.

Frustrated by this experience, Marsh determined to develop a better test for arsenic based on its separation as a volatile gaseous compound rather than as a solid precipitate. He first published his new test in 1836 (2) and, because it addressed an important forensic problem, his paper was rapidly translated into both German (3) and French (4). His original apparatus (figures 2 and 3) consisted of a U-tube with unequal arm lengths and a stopcock fitted to the shorter arm. With the stopcock in the open position, a piece of zinc [Zn] was placed in the shorter arm and the tube filled with dilute sulfuric acid [$\text{H}_2(\text{SO}_4)$] up to the stopcock in order to displace any air, both reagents having been previously tested to ensure that they were arsenic



Figure 3. Reproduction of a Marsh apparatus similar to that in figure 2 (Jensen-Thomas Apparatus Collection). A short section of glass tubing is placed in the bend of the U-tube in order to keep the rod of Zn metal in the short arm.

free. With the stopcock now in the closed position, the forensic sample to be tested was then added to the liquid. If arsenic was present in the sample, the ensuing reaction would generate a mixture of flammable dihydrogen gas [H₂] and trihydrogen arsenide or arsine gas [H₃As], which would accumulate below the stopcock



Figure 4. Marie-Fortunée Lefarge (1816-1852).

and force the liquid up the taller arm of the U-tube (5). When sufficient gas had formed, the stopcock was opened once again and the gases, under the hydrostatic pressure of the liquid column in the tall arm, were forced out the nozzle where they were ignited and the interior of the resulting flame allowed to play on a square of glazed ceramic or, better still, on the bottom of a glazed ceramic dish filled with cold water. If H₃As(g), and hence arsenic, was present, a black mirror of elemental arsenic would deposit on the bottom of the dish.



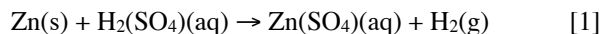
Figure 5. Mathieu Joseph Bonaventure Orfila (1787-1853).

Legal Vindication of the Marsh Test

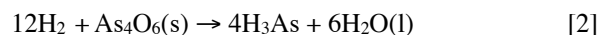
Because the arsenic in the Marsh test was separated from the forensic sample in the form of a gas, the complications that had plagued earlier precipitation tests were avoided and it soon became the definitive procedure for the forensic detection of arsenic. It was first employed in France during the 1840 trial of an attractive young widow by the name of Marie-Fortunée Lefarge (figure 4), who was accused of poisoning her much older husband, Charles, with arsenic that she had allegedly purchased for the purpose of killing rats (6). The trial was closely followed by the French press, especially when several faulty attempts to detect arsenic in Charles' body using the new Marsh test proved negative, only to be subsequently overturned when repeated by the famous toxicologist, Mathieu Orfila (figure 5), who had been originally hired as an expert witness by the defense! In the end Marie was found guilty and the Marsh test both legally and publicly vindicated.

The Chemistry of the Marsh Test Reconsidered

Rather surprisingly the chemistry underlying this historically important test appears to have been incorrectly rationalized for most of its history. According to this traditional interpretation, the zinc and sulfuric acid first react to produce dihydrogen gas:



which then reduces the tetraarsenic hexaoxide to trihydrogen arsenide and water (7):

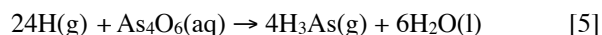
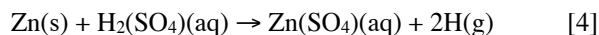


followed by the partial oxidation of the trihydrogen arsenide in the interior of the burning flame:



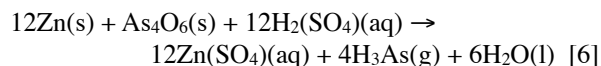
The only problem with this scenario is that, while steps 1 and 3 are both thermodynamically allowed ($\Delta G^\circ = -147.16 \text{ kJ/mol rx}$ and $-1.7 \times 10^3 \text{ kJ/mol rx}$ respectively), step 2 is thermodynamically disallowed ($\Delta G^\circ = +3.62 \text{ kJ/mol rx}$) (8). Indeed, it was known by the early 19th century that $\text{As}_4\text{O}_6(\text{s})$ cannot be directly reduced to $\text{H}_3\text{As}(\text{g})$ using $\text{H}_2(\text{g})$, though it is apparently so reduced when the $\text{H}_2(\text{g})$ is generated *in situ* within the Marsh apparatus. This led to the further speculation that freshly generated or “nascent” hydrogen gas differed in some way from regular hydrogen gas, thereby allowing it to undergo reactions not observed for the bulk form of the gas.

While the observation that freshly generated gases are often more reactive than bulk gases is an experimentally verifiable fact, its proper theoretical rationale is a different matter altogether. Thus an historical review of the nascent state concept uncovered a bewildering array of alternative theories, as well as experimental data suggesting that the effect is in fact kinetic rather than thermodynamic in nature (9). Nevertheless, the earliest and most persistent of these rationales, as well as the one most commonly invoked to explain the Marsh reaction in both 19th- and 20th-century textbooks (10), is the theory that freshly generated gases are initially monoatomic and that these transient free atoms only later combine with one another to produce the experimentally observed diatomic gas. Thus reactions 1 and 2 become instead:



Unlike reaction 2, reaction 5 is thermodynamically allowed ($\Delta G^\circ = -4.87 \times 10^3 \text{ kJ/mol rx}$). Unfortunately, however, reaction 4, unlike reaction 1, is now thermodynamically disallowed ($\Delta G^\circ = +259.34 \text{ kJ/mol rx}$) and thus our thermodynamic objections to the proposed mechanism remain.

From time to time an alternative proposal has appeared in the textbooks in which $\text{Zn}(\text{s})$, rather than either $\text{H}_2(\text{g})$ or $\text{H}(\text{g})$, is considered to be the active reducing agent (11):



The thermodynamics of this reaction are overwhelmingly favorable ($\Delta G^\circ = -1.76 \times 10^3 \text{ kJ/mol rx}$) and involve the oxidation of Zn from 0 to II and the reduction of As from III to -III. In this interpretation not only is hydrogen not the active reducing agent, reaction 1 is now relegated to the status of an unavoidable competing side-reaction resulting from the fact that both $\text{Zn}(\text{s})$ and $\text{H}_2(\text{SO}_4)(\text{aq})$ are required to be simultaneously present in the reaction mixture in order to facilitate reaction 6.

Later Developments

The original U-tube apparatus designed by Marsh continued to be sold by apparatus dealers well into the second decade of the 20th century (12). However, in 1837 the famous Swedish chemist, Jöns Berzelius, proposed an alternative version (figures 6-7) in which the sample to be tested was mixed with the $\text{Zn}(\text{s})$ and $\text{H}_2(\text{SO}_4)(\text{aq})$ in either a conventional gas-generating bottle or a two-necked Woulfe bottle and the resulting $\text{H}_3\text{As}(\text{g})$ passed through a tube that was divided into two sections by a narrow constriction that was strongly heated with an alcohol lamp or gas burner

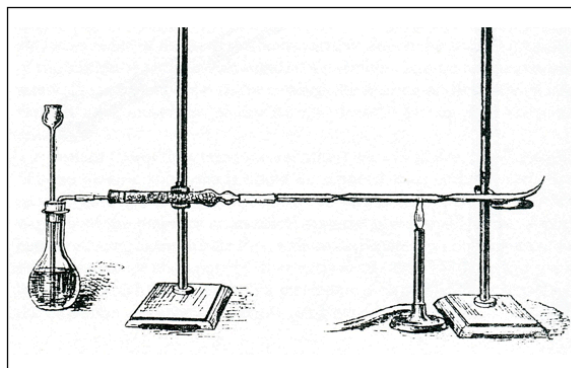
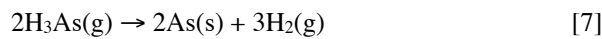


Figure 6. A version of Marsh's apparatus based on modifications introduced by Berzelius in 1837.



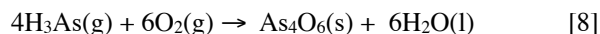
Figure 7. A reproduction of Berzelius' modification of the Marsh apparatus similar to that in figure 6 (Jensen-Thomas Apparatus Collection).

(13). The $\text{H}_3\text{As}(\text{g})$ was decomposed on passing through this heated constriction according to the equation:



and the $\text{As}(\text{s})$ deposited as a mirror in the second section. The accompanying $\text{H}_2(\text{g})$ was still burned off at the end of the tube, presumably to prevent any undecomposed $\text{H}_3\text{As}(\text{g})$ from escaping into the room. Since reaction 7 is thermodynamically favored at room temperature ($\Delta G^\circ = -137.8 \text{ kJ/mol rx}$), $\text{H}_3\text{As}(\text{g})$ must exist only because it is kinetically metastable, thus implying that the purpose of the heat source is to provide the necessary activation energy for its otherwise thermodynamically spontaneous decomposition. Because the decomposition or thermolysis tube could be weighed before and after deposition of the arsenic mirror, Berzelius' modification also allowed for partial quantification of the test. By the 1920s various versions of this alternative – often with a CaCl_2 drying tube inserted between the gas generator and the thermolysis tube – had completely displaced Marsh's original apparatus.

Yet a third variation of the Marsh test (figure 8) was to eliminate the thermolysis tube in Berzelius' apparatus and instead connect the gas-generating bottle directly to a simple delivery tube with a turned up end or jet for ignition of the evolved $\text{H}_3\text{As}(\text{g})$. In this case, the latter was allowed to oxidize completely to $\text{As}_4\text{O}_6(\text{s})$



which was then collected in a small test tube held above (rather than within) the flame, followed by confirmation tests using standard precipitation reactions for arsenic. Since the arsenic had been completely separated from the organic constituents of the forensic sample, these tests could now be performed without fear of coprecipitation.

The Marsh Test in Fiction

By the early 20th century the Marsh test was sufficiently well-known so as to make an appearance in several popular detective stories. In particular, it is mentioned in Dorothy L. Sayers' 1930 novel *Strong Poison*, where it is performed by Lord Peter Wimsey's manservant, Bunter. In keeping with the date, the procedure employed is actually Berzelius' thermolysis modification of the original test. Unfortunately Sayers left out some key information on the reagents used and so leaves the reader with the false impression that the test was done in boiling water (14):

In a small apartment usually devoted to Bunter's photographic work and furnished with a sink, a bench and a bunsen burner, stood the apparatus necessary for making a Marsh's test of arsenic. The distilled water was already bubbling gently in the flask, and Bunter lifted the little glass tube which lay across the flame of the burner.

"You will perceive my lord," he observed, "that the apparatus is free from contamination."

... Bunter [then] dropped the white powder into the wide mouth of the flask. All five heads eagerly bent



Figure 8. A rather cartoonish circa 1855 etching from the *Illustrated London News* depicting Dr. Alfred Swaine Taylor (on the left) – the so-called “father of British medical jurisprudence” – performing yet a third variation of the Marsh test in which the H_3As is completely oxidized to As_4O_6 .

THE MARSH TEST

over the apparatus. And presently, definitely, magically, a thin silver stain began to form in the tube where the flame impinged upon it. Second by second it spread and darkened to a deep brownish-black ring with a shining metallic center.

... "Is that arsenic?" breathed Miss Murchison, gently.

"I hope so," said Whimsey, gently detaching the tube and holding it up to the light. "It is either arsenic or antimony."

"Allow me, my lord. The addition of a small quantity of solute chlorinated lime should decide the question beyond reach of cavil,"

He performed this further test amid an anxious silence. The stain dissolved out and vanished under the bleaching solution.

"Then it is arsenic," said Parker.

"Oh yes," said Whimsey nonchalantly, "of course it is arsenic. Didn't I tell you?" His voice wavered a little with suppressed triumph.

Actually a far better description of the Marsh test is given in R. Austin Freeman's 1923 detective novel, *The Cat's Eye*, which features his well-known scientific detective, Dr. John Evelyn Thorndyke (figure 9). The test is performed with the help of Thorndyke's manservant and laboratory assistant, Polton, on a sample of poisoned chocolate (15, 16):

"And now we will try the most definite and conclusive test of all – Marsh's." He turned to the other apparatus which Polton had made ready, which consisted of a squat bottle with two short necks, through one of which passed a tall glass funnel, and through the other a glass tube fitted with a tap and terminating in a fine jet. The contents of the bottle – lumps of zinc immersed in sulphuric acid – were effervescing briskly, and the tap was turned on to allow the gas to escape through the jet. To the latter Polton now applied a lighted match, and immediately there appeared a little pale violet flame. Picking up a white tile that had been placed in readiness, Thorndyke held it for a moment in the flame and then looked at it.

"You see," said he, "that the tile is quite unsoiled. If there had been the smallest trace of arsenic in the bottle, a dark spot would have appeared on the tile. So we may take it that our chemicals are free from arsenic. Now let us try the solution of the sweet."

He took up the beaker containing the solution of disintegrated chocolate, and poured very slowly, drop by drop, about a teaspoon into the funnel of the bottle. Then, after giving it time to mix thoroughly with the other contents, he once more picked up the tile and held it for an instance in the flame. The result was, to

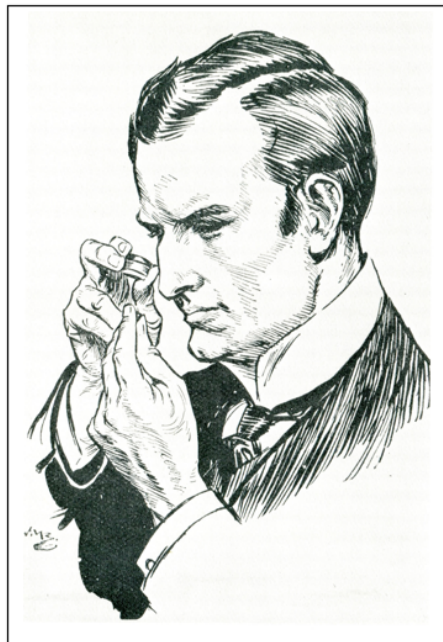


Figure 9. R. Austin Freeman's great scientific detective, Dr. John Evelyn Thorndyke, as depicted in a 1908 drawing from *Pearson's Magazine*.

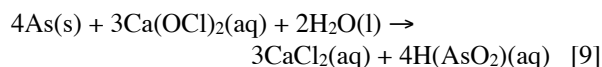
me, most striking. In the very moment when the tile touched the flame, there appeared on the white surface a circular spot, black, lustrous, and metallic.

"That," said Thorndyke, "must be either antimony or arsenic. By its appearance it is obviously metallic arsenic, but still we will make a differential test. If it is arsenic it will dissolve in a solution of chlorinated lime; if it is antimony it will not." He removed a stopper from a bottle labelled "Chlorinated Lime," and poured a little pool of the solution on the tile. Almost immediately the black spot began to fade at the edges, and to grow smaller and fainter until at length it disappeared altogether. "That completes our inquiry," said Thorndyke as he laid down the tile.

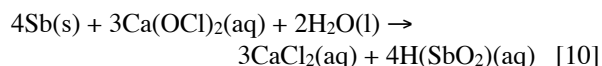
This account is actually preceded by a description of various preliminary qualitative tests for arsenic, including its precipitation as yellow diarsenic trisulfide [As₂S₃], as green copper hydrogen arsenite [CuH(AsO₃)], and its deposition on copper metal (Reinsch's test). The accuracy of Freeman's descriptions is doubtlessly due to the fact that he maintained a private workshop/laboratory in his home in which he personally replicated all of the forensic tests performed by his fictional detective (17).

Like its close analog in the periodic table, antimony [Sb], if present in the forensic sample, will also deposit a metallic mirror during the Marsh test and testing of the mirror with the aqueous solution of chlo-

minated lime or calcium hypochlorite [Ca(OCl)₂] used by both Bunter and Thorndyke was necessary in order to distinguish between the two deposits. The net reaction in question would appear to be:



in which arsenic is oxidized from 0 to III and chlorine is reduced from I to -I. However, from a thermodynamic standpoint it is not readily understandable why reaction 9 works for As(s) but the analogous reaction for Sb(s) does not:



since H(SbO₂)(aq) is thermodynamically more stable than H(AsO₂)(aq) (8).

Today the Marsh test is largely an historical relic and is unlikely to appear in modern detective novels other than those deliberately set in the past. Like most analytical procedures based on wet chemistry, it was gradually displaced, starting in the 1960s, by more modern instrumental methods of analysis, and especially by the detection of arsenic using either atomic absorption spectrometry or neutron activation analysis (1).

References and Notes

1. Previous historical treatments of the history of arsenic testing include S. H. Webster, "The Development of the Marsh Test," *J. Chem. Educ.*, **1947**, *24*, 487-490; W. A. Campbell, "Some Landmarks in the History of Arsenic Testing," *Chem. Brit.*, **1965**, *1*, 198-201; and R. H. Goldsmith, "The Search for Arsenic," in S. Gerber, R. Saferstein, Eds., *More Chemistry and Crime*, ACS Books: Washington, DC, 1997, pp. 149-168. More superficial accounts appear in P. Macinnis, *Poisons: From Hemlock to Botox and the Killer Bean of Calabar*, Arcade: New York, NY, 2004, pp. 72-73; K. Watson, *Poisoned Lives: English Poisoners and their Victims*, Hambledon & London: London, 2004, pp. 16-20; J. Emsley, *The Elements of Murder: A History of Poison*, Oxford University Press: Oxford, 2005, pp. 149-151; and J. Parascandola, *King of Poisons: A History of Arsenic*, Potomac Books: Washington, DC, 2012, pp. 10-12.
2. J. Marsh, "An Account of a Method of Separating Small Quantities of Arsenic from Substances with which It May Be Mixed," *Edinburgh New Phil. J.*, **1836**, *21*, 229-236.
3. J. Marsh, "Beschreibung eines neuen Verfahrens um kleine Quantitäten Arsenik von den Substanzen abzuschneiden, womit er gemischt ist," *Ann. Chem.*, **1837**, *23*, 207-227. This includes two appended editorial commentaries on the paper.
4. J. Marsh, "Arsenic; nouveau procédé pour le découvrir dans les substances auxquelles il est mêlé," *J. Pharm.*, **1837**, *23*, 553-562.
5. There seems to be an ambiguity in the chemical literature as to whether arsine should be represented as trihydrogen arsenide or as arsenic trihydride. Electronegativity scales are not helpful as some give As an EN value less than H (Pauling), some an EN value greater than H (Sanderson), and some an EN value equal to H (Allred-Rochow). However, the assumption of both equations 2 and 6 is that the arsenic is reduced from III to -III which is consistent with the trihydrogen arsenide interpretation.
6. There are many summaries of the Lafarge trial. See, for example, C. J. S. Thompson, *Poison Mysteries in History, Romance and Crime*, Lippincott: Philadelphia, PA, 1924, pp. 273-278. Madame Lafarge's own version of events appears in her autobiography, M. F. Lafarge, *Memoirs of Madame Lafarge Written by Herself*, Carey & Hart: Philadelphia, PA, 1841. Both Thompson and, of course, Lafarge herself contend that she was innocent.
7. As₄O₆(s) is slightly soluble in water where it eventually hydrolyzes to either H(AsO₂)(aq) or H₃(AsO₃)(aq). However these reactions are very slow, suggesting that the rapid reduction in the Marsh apparatus involves suspended particles of As₄O₆(s) instead.
8. All thermodynamic data are from A. J. Bard, R. Parsons, J. Jordan, Eds., *Standard Potentials in Aqueous Solution*, Dekker: New York, NY, 1985.
9. W. B. Jensen, "Whatever Happened to the Nascent State?," *Bull. Hist. Chem.*, **1990**, *6*, 26-36.
10. For a recent example invoking nascent hydrogen, see N. Wiberg, *Inorganic Chemistry*, Academic Press: New York, NY, 2001, pp. 744-745.
11. C. Bloxam, *Chemistry, Inorganic and Organic, with Experiments*, Lea: Philadelphia, PA, 1873, p. 279.
12. See for example, *Scientific Materials Blue Book: Equipment and Supplies for Chemical, Metallurgical and Biological Laboratories*, Scientific Materials: Pittsburgh, PA, 1919, p. 14, Item 232.
13. J. Berzelius, "Paton's, Marsh's und Simon's Methoden Arsenik zu entdecken," *Pogg. Ann. Phys. Chem.*, **1837**, *42 (2nd series)*, 159-163.
14. D. L. Sayers, *Strong Poison*, Harper & Row: New York, NY, 1930, pp. 304-305, 315-318.
15. R. A. Freeman, *The Cat's Eye*, Burt: New York, NY, 1927, pp. 163-167. First British edition 1923.
16. An even earlier description of the Marsh test occurs in the short story, "The Moabite Cipher," which appears in R. A. Freeman, *John Thorndyke's Cases*, Chatto & Windus: London, 1909. First American edition 1931.
17. N. Donaldson, *In Search of Dr. Thorndyke: The Story of R. Austin Freeman's Great Scientific Investigator and his Creator*, Bowling Green University Popular Press: Bowling Green, OH, 1971, p. 154.