

METHODS OF DETERMINING THE COMPOSITION OF AMALGAMS.

M. G. MELLON, Purdue University.

While working with lead amalgams, it became necessary to make a search of the entire literature relating to the scientific study of amalgams in order to ascertain what methods have been used in determining their quantitative composition. Since the titles and the abstracts of the articles found rarely indicated anything concerning analytical methods, the papers themselves had to be read. It is hoped this bibliography may save others a similar expenditure of time.

More than 850 references were found, of which about 75 per cent were read. The remainder could not be consulted because of inaccessibility, incorrect statements of the reference, or unfamiliar languages, such as Russian, Scandinavian and Dutch. It is believed, however, that the present report is fairly complete.

Although the earlier references of this list go back to 1750, little of value was located until the work of Davy in 1808. In many cases the amalgams were stated to have a given composition, but no method of analysis was given. No effort was made to locate every reference mentioning incidental uses of amalgams, such as their application in certain physico-chemical measurements and in organic chemistry as reducing agents, or to cover their industrial application in such operations as metallurgy, electrochemistry and dentistry. No mention is made of the cases in which the elements composing the amalgam were weighed directly and its composition calculated from these weights. Practically all the references deal with binary amalgams.

Types of Methods. The various procedures used in determining the composition of amalgams have been classified according to the following outline:

I. Gravimetric Methods—

1. Gas-evolution processes—those in which either the mercury or the other constituent was volatilized; or in which the amalgam reacted with a solution to evolve an amount of a gas equivalent to the element in the mercury. The amount of desired constituent was calculated from the weight of residue or from the volume of the evolved gas.

2. Gravimetric precipitation processes—those in which the desired constituent was separated and subsequently weighed in the form of an insoluble precipitate.

3. Solution and extraction processes—those in which one of the elements was dissolved out with an appropriate solvent. The element undissolved was weighed as such, or the one dissolved was determined by evaporating the extract to dryness under suitable conditions and weighing the residue.

II. Titrametric Methods—

1. Neutralization processes—those in which the desired constituent was dissolved out of the amalgam by means of water or an excess of a standard acid and the solution then titrated with an acid or base, respectively.

2. Oxidation-reduction processes—those in which the desired constituent was dissolved out and determined by means of a suitable oxidizing or reducing solution.

3. Titrametric precipitation processes—those in which the desired constituent was dissolved out and determined by means of a suitable solution forming a precipitate with the constituent.

III. Electrolytic Methods—

1. Direct processes—those in which the element was deposited upon an electrode in the usual manner and weighed.

2. Indirect processes—those in which the element was deposited in a weighed amount of mercury, the amount deposited being calculated according to Faraday's law from the weight or volume of some other element liberated in a coulometer placed in series in the same electrical circuit.

IV. Physico-Chemical Methods—

This group includes those processes involving the measurement of some physical property of the system investigated which is a function of the concentration of the desired constituent. Such properties of amalgams include density, electrode potential and color.

SUMMARIZED INFORMATION

Element Det'd	Method	Quantity Measured	References
NH ₃	Grav.—Gas.-Evol.....	NH ₃ H ₂	23, 44, 58, 77
	Grav.—Sol.-Extr.....		80
	Titration—Neutr.....	Vol.	59, 69
Al	Grav.—.....	Al ₂ O ₃	66, 102
	Grav.—Gas.-Evol.....	H ₂	102
As	Titration—Oxid-Red.....	Vol.	19
Ba	Grav.—Pptn.....	BaSO ₄	66, 83, 86
	Grav.—Pptn.....	BaCrO ₄	84
	Titration—Neutr.....	Vol.	89, 90, 103
Bi	Titration—Pptn.....	Vol.	93
	Grav.—Pptn.....	Bi ₂ O ₃	17
	Grav.—Sol.-Extr.....	Bi ₂ O ₃	34
Cd	Grav.—Pptn.....	CdO	7
	Grav.—Gas.-Evol.....	CdO	35
	Grav.—.....	CdO	96, 99
	Elec.—F's Law.....	Time-Amp.	13, 94, 97
	Phys-Chem.....	Density	32, 72
Cs	Phys-Chem.....	E.M.F.	57, 103
	Grav.—Pptn.....	Cs ₂ PtCl ₆	85, 87
	Titration—Neutr.....	Vol.	43, 89, 90, 103
Ca	Grav.—Pptn.....	CaO	79, 84
	Grav.—Gas.-Evol.....	CaO	28
	Titration—Neutr.....	Vol.	8, 89, 90, 103
	Titration—Pptn.....	Vol.	93

SUMMARIZED INFORMATION—Continued

Element Det'd	Method	Quantity Measured	References
Cr	Grav.—Gas-Evol.	Cr_2O_3	20
Co	Grav.—Gas-Evol.	Co	62
Cu	Grav.—Gas-Evol.	CuO	34, 73, 76
	Elec.—F's Law.	H_2	56
	Elec.—F's Law.	Ag	73, 76
	Elec.—F's Law.	Time-Amp.	94, 97
	Phys.—Chem.	Color	73, 76
Au	Grav.—Sol-Extr.	Au	10, 12, 96
	Grav.—Gas-Evol.	Au	101
	Phys-Chem.	E.M.F.	57
In	Elec.—F's Law.	Ag	76
Fe	Grav.—Gas-Evol.	Fe	62
	Grav.—Gas-Evol.	Fe_2O_3	73, 76
Pb	Grav.—Pptn.	PbSO_4	3, 26, 30, 34, 37
	Grav.—Pptn.	PbCrO_4	51, 53
	Grav.—Pptn.	PbO	96
	Elec.—F's Law.	Cu	52
	Elec.—F's Law.	Ag	54
	Elec.—F's Law.	Time-Amp.	94, 97
	Phys.—Chem.	E.M.F.	57, 103
Li	Grav.—Sol-Extr.	Li_2SO_4	84, 93
	Grav.—Sol-Extr.	LiCl	66
	Titration—Neutr.	Vol.	8, 40, 49, 73, 76, 89, 90, 103
Mg	Grav.—Pptn.	$\text{Mg}_2\text{P}_2\text{O}_7$	35, 40, 47, 84
Mn	Grav.—Gas-Evol.	Mn_2O_4	65
Hg	Grav.—Pptn.	HgS	3, 30
	Grav.—Pptn.	HgCl	19
	Grav.—Gas-Evol.	Hg	41, 62, 74
	Grav.—Sol-Extr.	Hg	11, 14, 16, 24, 26, 32, 35, 40, 42, 43, 49, 56, 60, 68, 78, 82, 93
	Titration—Oxid-Red.	Vol.	79
	Elec.—Directly.	Hg	61, 99
	Phys.—Chem.	Color	32
Mo	Grav.—Gas-Evol.	Mo	21
Os	Grav.—Gas-Evol.	Os	98
K	Grav.—Pptn.	K_2PtCl_6	9, 81, 83, 84, 85, 86, 87
	Grav.—Gas-Evol.	H_2	22, 26, 55
	Grav.—Sol-Extr.	KCl	66, 81, 88, 96, 100
	Grav.—Sol-Extr.	K_2SO_4	84, 85, 92
	Titration—Neutr.	Vol.	2, 5, 6, 40, 42, 45, 48, 49, 55, 68, 81, 88, 89, 90, 92, 93, 100, 103
Rb	Grav.—Pptn.	Rb_2PtCl_6	85, 87
	Titration—Neutr.	Vol.	40, 43, 89, 90, 103
Ag	Grav.—Pptn.	AgCl	61, 64, 67
	Grav.—Gas-Evol.	Ag	17, 34, 36, 38, 50, 67
Na	Grav.—Gas-Evol.	H_2	4, 22, 26, 55
	Grav.—Sol-Extr.	NaCl	66, 81, 88, 96, 100
	Grav.—Sol-Extr.	Na_2SO_4	82, 84, 85, 86
	Titration—Neutr.	Vol.	1, 2, 5, 6, 27, 39, 40, 45, 46, 49, 55, 63, 68, 70, 78, 81, 88, 89, 90, 91, 93, 100, 103
Sr	Grav.—Pptn.	SrSO_4	82, 84, 92
	Titration—Neutr.	Vol.	25, 89, 90, 91, 92, 103
	Titration—Pptn.	Vol.	93
Tl	Grav.—Pptn.	TlI	18, 35

SUMMARIZED INFORMATION—Continued

Element Det'd	Method	Quantity Measured	References
Sn	Titration—Neutr.....	Vol. *	71, 75
	Titration—Oxid-Red.....	Vol.	95
	Electro.—F's Law.....	Time-Amp.	94
	Electro.—F's Law.....	Ag	71, 76
	Phys.—Chem.....	E.M.F.	103
	Grav.—Pptn.....	SnO ₂	26, 30, 96, 99
	Grav.—Sol-Extr.....	SnO ₂	34
	Electro.—F's Law.....	Ag	76
Zn	Phys.—Chem.....	E.M.F.	103
	Grav.—Pptn.....	ZnO	15, 26, 40
	Extr.—Sol-Extr.....	ZnO	34
	Electro.—F's Law.....	Ag	29
	Electro.—F's Law.....	Time-Amp.	94, 97
	Phys.—Chem.....	E.M.F.	31, 33, 57, 103
	Phys.—Chem.....	Density	72

BIBLIOGRAPHY.

1. Allmand and Pollack. *J. Chem. Soc.* 115, 1,021 (1919).
2. Bain and Withrow. *J. Phys. Chem.* 25, 535 (1921).
3. Bauer. *Ber.* 4, 449 (1871).
4. Berl and Jurrissen. *Z. Angew. Chem.* 23, 248 (1909).
5. Berthelot. *Ann. Chim. Phys.* (5) 13, 433 (1879).
6. Berthelot. *Compt. Rend.* 88, 1,108 (1879).
7. Bijl. *Z. Phys. Chem.* 41, 641 (1902).
8. Bornemann. *Metallurgie* 9, 473 (1912).
9. Braley and Hall. *J. Am. Chem. Soc.* 42, 1,770 (1920).
10. Braley and Schneider. *Ibid.* 43, 740 (1921).
11. Cady. *J. Phys. Chem.* 2, 551 (1898); 3, 107 (1899).
12. Chester. *Am. J. Sci.* (3) 16, 24 (1878).
13. Cohen, Helderman and Mösveld. *Z. Phys. Chem.* 96, 259 (1920).
14. Cohen and Inouye. *Ibid.* 71, 625 (1910).
15. Cohen and Van Ginneken. *Ibid.* 75, 437 (1910).
16. Crenshaw. *J. Phys. Chem.* 14, 158 (1910).
17. Crockewit. *J. Prakt. Chem.* 45, 87 (1848).
18. Crookes. *J. Chem. Soc.* 17, 147 (1864).
19. Dumesnil. *Compt. Rend.* 152, 868 (1911).
20. Feree. *Ibid.* 121, 822 (1895).
21. Feree. *Ibid.* 122, 733 (1896).
22. Fernekes. *J. Phys. Chem.* 7, 611 (1903).
23. Gay-Lussac and Thenard. *Ann. Chim. Phys.* (1) 73, 197 (1810).
24. Griffin. *Technical Methods of Analysis*, 163 (1921).
25. Guntz and Roederer. *Bull. Sec. Chim.* (3) 35, 494 (1906).
26. Guthrie. *Phil. Mag.* (5) 16, 321 (1883).
27. Haber and Sack. *Z. Elektrochem.* 8, 250 (1902).
28. Hare. *Am. J. Sci.* 40, 293 (1841).

29. Henderson. *Phys. Rev.* 29, 507 (1909).
30. Horsford. *Am. J. Sci.* (2) 13, 305 (1852).
31. Hulett. *Phys. Rev.* 33, 307 (1911).
32. Hulett and DeLury. *J. Am. Chem. Soc.* 30, 1805 (1908).
33. Hulett and Minchin. 21, 391 (1906).
34. Humphreys. *J. Chem. Soc.* 69, 243 (1896).
35. Humphreys. *Ibid.* 69, 1,679 (1896).
36. Hünefeld. *Schweigger's Ann.* 61, 125 (1831).
37. Jordan. *J. Prakt. Chem.* 10, 439 (1837).
38. Joule. *J. Chem. Soc.* 16, 378 (1863).
39. Kerp. *Z. Anorg. Chem.* 17, 284 (1898).
40. Kerp, Böttger, Winter and Iggena. *Ibid.* 25, 1 (1900).
41. Koenig. *J. Prakt. Chem.* 70, 64 (1857).
42. Kurnakoff. *Z. Anorg. Chem.* 23, 439 (1900).
43. Kurnakoff and Zukowsky. *Ibid.* 52, 416 (1907).
44. Landolt. *Ann. Suppl.* 6, 346 (1868).
45. Lewis, Adams and Lanman. *J. Am. Chem. Soc.* 37, 2,656 (1915).
46. Lewis and Kraus. *Ibid.* 32, 1,459 (1910).
47. Loomis. *Ibid.* 44, 8 (1922).
48. MacInnes and Parker. *Ibid.* 37, 1,451 (1915).
49. Maey. *Z. Phys. Chem.* 29, 119 (1899).
50. Maey. *Ibid.* 50, 209 (1905).
51. Mellon. *J. Am. Chem. Soc.* 44, 2,167 (1922).
52. Mellon and Henderson. *J. Am. Chem. Soc.* 42, 676 (1920).
53. Mellon and Reinhard. *Proc. Ind. Acad. Sci.* 31, 189 (1921).
54. Mellon and Reinhard. *Ibid.* 31, 181 (1921).
55. Merz and Weith. *Ber.* 14, 1,438 (1881).
56. Meyer. *Z. Phys. Chem.* 7, 477 (1891).
57. Meyer. *Wied. Ann.* 61, 225 (1897).
58. Moissan. *Compt. Rend.* 133, 803 (1901).
59. Moissan. *Bull. Soc. Chim.* (3) 27, 717 (1902).
60. Müller. *Metallurgie* 7, 738 (1910).
61. Müller and Hönig. *Z. Anorg. Chem.* 121, 344 (1922).
62. Nagaoka. *Wied. Ann.* 59, 66 (1896).
63. Neuhausen. *J. Am. Chem. Soc.* 44, 1,411 (1922).
64. Ogg. *Z. Phys. Chem.* 27, 285 (1898).
65. Prelinger. *Monatsh.* 14, 353 (1893).
66. Ramsay. *J. Chem. Soc.* 55, 521 (1889).
67. Reinders. *Z. Phys. Chem.* 54, 609 (1906).
68. Reuter. *Z. Elektrochem.* 8, 801 (1902).
69. Rich and Travers. *J. Chem. Soc.* 89, 872 (1906).
70. Richards and Conant. *J. Am. Chem. Soc.* 44, 601 (1922).
71. Richards and Daniels. *Ibid.* 41, 1,732 (1919).
72. Richards and Forbes. *Carneg. Inst. Pub.* 56, 1 (1906); *Z. Phys. Chem.* 58, 690 (1907).
73. Richards and Garrod-Thomas. *Z. Phys. Chem.* 72, 165 (1910).
74. Richards and Singer. *J. Am. Chem. Soc.* 26, 300 (1904).
75. Richards and Smyth. *Ibid.* 44, 524 (1922); 45, 1,455 (1923).

76. Richards, Wilson and Garrod-Thomas. *Carneg. Inst. Pub.* 118, 1 (1909).
77. Routledge. *Chem. News.* 26, 210 (1872).
78. Sack. *Z. Anorg. Chem.* 34, 286 (1903).
79. Schürger. *Ibid.* 25, 425 (1900).
80. Smith. *J. Am. Chem. Soc.* 29, 844 (1907).
81. Smith. *Ibid.* 39, 179 (1917).
82. Smith. *Ibid.* 39, 1,545 (1917).
83. Smith. *Ber.* 40, 2,941 (1907).
84. Smith. *Am. Chem. J.* 37, 506 (1907).
85. Smith. *Ibid.* 38, 671 (1908).
86. Smith. *J. Phys. Chem.* 9, 13 (1905).
87. Smith. *Z. Anorg. Chem.* 58, 381 (1908).
88. Smith and Ball. *J. Am. Chem. Soc.* 39, 179 (1917).
89. Smith and Bennett. *Ibid.* 31, 799 (1909).
90. Smith and Bennett. *Ibid.* 32, 622 (1910).
91. Smith and Braley. *Ibid.* 39, 1,545 (1917).
92. Smith and Rees. *Ibid.* 40, 1,802 (1918).
93. Smith and Withrow. *Ibid.* 29, 321 (1907).
94. Spencer. *Z. Elektrochem.* 11, 681 (1905).
95. Sucheni. *Ibid.* 12, 726 (1906).
96. Tammann. *Z. Phys. Chem.* 3, 441 (1889).
97. Tammann and Jander. *Z. Anorg. Chem.* 124, 105 (1922).
98. Tenet. *Trans. Roy. Soc.* 94, 418 (1804).
99. Van Heteren. *Z. Anorg. Chem.* 42, 129 (1904).
100. Wells and Smith. *J. Am. Chem. Soc.* 42, 185 (1920).
101. Wilm. *Z. Anorg. Chem.* 4, 325 (1893).
102. Wislicenus and Kauffmann. *Ber.* 28, 1,323 (1895).
103. Wogau. *Ann. Physik.* 23, 345 (1907).