sulfuric acid and the temperature of the system. The end-point, however, is definite and cannot be overstepped. The presence of the asbestos is no objection.

SUMMARY

A method for the analysis of Paris green is proposed by which the copper is precipitated as the oxalate and the oxalic acid combined is titrated with permanganate, the arsenic being oxidized in the filtrate by iodine after being made alkaline. The procedure is accurate and, with the exception of the fact that the copper oxalate must stand over night, rapid.

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THE DETERMINATION OF SULFUR IN IRON AND STEEL

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In 1904, Hendrixson announced¹ that iron dissolves easily in chloric acid, going quantitatively to the ferric condition. At that time the author was studying the methods for the determination of sulfur in iron and steel and at once recognized the possibility of using chloric acid as the solvent in the analysis.

Chloric acid is a highly satisfactory solvent for the usual finely granular material used for analysis; the action takes place rapidly and with far less gas evolution than when nitric acid is the solvent. In attempting quantitative data on samples of known

prints and through the microscope the actual condition is far more truthfully revealed than from the reports of the analyst who may rely on one single result or unwittingly fail to indicate the diversity of his check determinations.

The statistical method of studying the distribution of results would be highly illuminating but is hardly practical because of the material, time and labor required. In no case on the samples here studied were less than duplicate results obtained; often 3 and in several cases 6 or 7 determinations were run for the sake of establishing a mean value of the sulfur content.

PREPARATION OF SAMPLE

We suppose that sulfur occurs in our materials as sulfide of iron, sulfide of manganese, or indeed as a double sulfide of the two. These sulfides are probably quite insoluble in the more common α - and β -modifications of ferrite for we have no difficulty in discovering the particles with the microscope when only a few hundredths of one per cent of sulfur are present in the metal. This discrete occurrence of sulfur in the metal, and in particular its segregation in that portion of an ingot which solidifies last is perfectly well known to metallurgists and metallographers. The bearing of this on the results obtained by the analyst is highly significant. Even more imperative is its dictum regarding the preparation of the sample.

In a 5-g. sample of metal it requires about 0.0005

FIG. I—SULFUR PRINT OF CAST IRON INGOT

FIG. II—SULFUR PRINT OF STEEL SHAFTING

sulfur content the work developed largely into a study of the uniformity of samples, the nitric acid and fusion methods, the precision of results and the work of others.

A limited number of analyses by the new method indicate the difficulties and possibilities of its use.

From the analytical point of view the segregation of sulfur in the ferrous materials was first mentioned by Eggertz in 1868;² our Bureau of Standards has frequently related its difficulties along the same line, while Bauer and Deiss³ take particular pains to expound the difficulty and indicate how the analyst shall avoid falling into serious error.

This segregation of sulfur is a well known condition to the metallurgist and metallographer; with sulfur

g. of sulfur or 0.00014 g. FeS or MnS to influence the analysis by 0.001 per cent. This is represented by a cube of the substance 0.3 mm. on a side; such a particle will barely pass a 50-mesh screen. For some degree of safety, then, the material should pass an 80-mesh screen and be thoroughly mixed; this material would be uniform to about 0.001 per cent, in 5-g. lots. The actual loss of sulfur by such treatment awaits investigation. Variations due to analytical conditions might still cause deviations.

Figs. I to IV visualize this common characteristic of materials. Fig. I is a full-size sulfur print made by photographic paper on a small ingot of cast iron. It shows the spots of sulfide throughout the entire section and, in particular, the layer at the top which is extremely high in sulfur. The accurate sampling of such an ingot is obviously quite a task.

Analyses of crushed millings gave the following results:

¹ *J. Am. Chem. Soc.*, **26** (1904), 747.

² *Chem. News*, **18** (1868), 15.

³ "Sampling and Chemical Analysis of Iron and Steel," translated by Hall and Williams, 1915.

TABLE I—PERCENTAGES OF SULFUR

Original Crushed Millings	AFTER GRINDING	
	20 to 100 mesh	Through 100 mesh
0.171	0.171	0.164
0.176	0.171	0.165
0.176	0.171	0.167
0.182	0.174	...
0.182	0.174	...
0.184	0.175	...
0.184	0.177	...
0.194	0.177	...
0.197	...	...
0.201	...	...

Some of the material which persisted coarsely granular even after the twenty passes through the disc grinder was probably high in sulfur although small in amount.

Fig. II is another sulfur print of a section of shafting showing high sulfur spots. Figs. III and IV are photomicrographs of this material at 200 diameters, suitably etched. The two prints were of spots a bare half-inch apart on the metal surface. Fig. III shows fine, practically sulfur-free metal; Fig. IV shows typical sulfides. Each cube the size of the dark spot would put 0.001 per cent of sulfur in a 5-g. sample. Remembering that the entire area of Fig. IV represents an actual surface of only 0.16 sq. mm. and is just a trifle too large to pass a 50-mesh screen we are naturally not surprised that the results of analyses on coarse turnings varied from 0.06 to 0.09 per cent sulfur.

For real precision the analyst can best determine the *limits* of the sulfur range on the weight of sample and fineness selected. The average result is, of course, the best value available. The fallacy of any selection which sorts out one size of particle is plain; nothing could be more untechnical than to pound the material and screen out a portion for analysis. The great objective is how to reduce a lot to the desired size; at the present moment there is no light on the difficulty.

METHODS OF ANALYSIS

A perusal of the accompanying bibliography in the original allows one to classify the methods for sulfur determination according to the following scheme:

- I—Direct combustion in oxygen.
- II—Volatilization as SCl_2 in chlorine at red heat.
- III—Volatilization with H_2 and CO_2 at red heat as H_2S .
- IV—Fusion of powdered sample with oxidizing alkaline salts; sintering of powder with MgO and NaOH .
- V—Oxidizing both iron and sulfur with acid solution (or halogen); precipitation of sulfur direct or after various manipulations.
 - A—Bromine.
 - B—Concentrated HNO_3 .
 - C— KClO_3 and HCl .
 - D—Aqua regia.
 - E—Bromine and HCl .
 - F— HNO_3 and KClO_3 and KBr .
 - G—Chloric acid.
- VI—Nitric acid solution and fusion of the evaporated mass.
- VII—Solution of iron leaving sulfur and sulfides ready to filter off and oxidize by acids or fusion.
 - A—Ferric chloride solution.
 - B—Copper-alkali (Na , K , or NH_4)-chloride solution.
- VIII—Sulfur evolved as H_2S with H_2SO_4 , or HCl , or both.
 - A— H_2S oxidized to H_2SO_4 direct or after precipitation of a metal, weighing as BaSO_4 . Oxidation by:
 - 1—Bromine.
 - 2—Chlorine.
 - 3—Permanganate.

- 4—Hydrogen peroxide.
- 5—Sodium peroxide.
- 6—Lead peroxide.
- 7—Hydrogen flame and permanganate.

B— H_2S determined volumetrically.

- 1—Iodine titer directly.
- 2—Iodine in excess and back with thio-sulfate.
- 3—Iodine liberated by KMnO_4 , back with thiosulfate.
- 4—Direct titer with KMnO_4 .
- (Absorbents for these 4 are NaOH , KOH , salts of Pb , Cd and Zn)
- 5— FeCl_3 is reduced to FeCl_2 and run back with $\text{K}_2\text{Cr}_2\text{O}_7$.
- 6— ZnS reduces Fe^{+++} to Fe^{++} and back with KMnO_4 .
- 7—Absorb in NaOH and titrate with $\text{Pb}(\text{NO}_3)_2$.
- 8—Absorb in standard arsenite and back with iodine.
- 9—Absorb in AgNO_3 to AgS and KSCN titer.

C— H_2S determined gravimetrically, weigh as CuO , AgS , Ag , As_2O_3 or BaSO_4 .

D—Colorimetric determination of H_2S .

- 1—Use a Pb salt.
- 2— Cd salt gives CdS .
- 3—Absorb in As_2O_3 solution.
- 4—Formation of methylene blue.
- 5—Gives color to metal foil.

E— H_2S precipitates PbS , to be read in graduated tube after whirling.

Concerning these methods of analysis a few explanatory remarks will indicate their relative importance and certain conditions of use.

Method I has been abandoned, after trial, except for particular ferro-alloys.

Method II is justly dismissed without comment.

Method III has some figures to substantiate it, but has too many inherent difficulties.

Method IV has been supported by considerable evidence of accuracy and by several workers. The material is best very finely powdered, a serious objection. Manipulation may also be objected to. Extremely slight practical use apparently attaches to the method.

Method V is widely used in one or another form, especially for more precise work. Nitric acid used as solvent must be replaced by hydrochloric and the silica is best rendered insoluble by baking. The ferric chloride may be separated by ether or the iron may be precipitated with ammonia and either the sulfuric acid washed out of the hydroxide or the hydroxide dissolved out of the already precipitated barium sulfate. Ferric iron may be reduced to ferrous by a variety of reagents or the same prevented from entering the barium sulfate precipitate by using organic substances to form complex ions unaffected by the precipitation. Residues remaining after the acid treatment of the original sample may get special attention and the sulfur recovered added to the main portion.

This method has been abundantly disparaged and can, of course, be proven inadequate by uncritical operators. On the other hand, the method has been substantiated by abundance of the best work and nothing less than fresh evidence can shake it. The precipitation of the barium sulfate in the ferric chloride solution has been checked as accurate by workers of

FIG. III $\times 200$ —SECTION OF STEEL SHAFTING
FINE, PRACTICALLY SULFUR-FREE METAL

FIG. IV $\times 200$ —SECTION HALF INCH DISTANT FROM FIG. III
STEEL ROTTEN WITH SULFIDES

six nations. A table covering this point is offered in this paper as bearing directly and unequivocally on this point.

Method VI is generally considered an excellent control method.

Method VII is both old and new and theoretically excellent; the slowness of solution is always against it.

Method VIII has received by far the most attention from earliest to latest times, as the history of sulfur determination ranges. Samples may be annealed before dissolving, without or with admixed reagents. The evolution may be effected by acid alone or in the presence of hydrogen or carbon dioxide, or both. The gases may be passed through a red hot tube. The residue may be oxidized wet or by fusion or treated with hydrogen and hydrochloric acid at a red heat, any recovery being added to the main portion. The cumulative evidence is that quick evolution with concentrated hydrochloric acid gives a close approximation if not the exact sulfur content. Only in unusual cases will sulfur persist in the residue.

The author has experimented considerably with this method but delays results for a later communication.

A complete review and digest of the whole subject is needed but requires far more space than the importance of the subject would warrant.

As other workers have established the accuracy of the nitric acid method by attempting to measure or recover barium sulfate from the filtrate, a procedure always liable to renewed error through impurities and the environment, the author ran a series of 28 lots simply to establish the actual recovery on a measured amount of sodium sulfate. Every condi-

tion closely approached that of an actual analysis.

The ferric chloride solution was made by dissolving 560 g. of the pure solid salt in 2 liters of water, filtering and using 50 cc. in each case.

The sodium sulfate solution was made by dissolving 1.220 g. of the pure fused salt in 1 liter of water: 10 cc. were taken in each instance with a pipette delivering 9.996 cc., temperature corrected. All determinations were made at the same time with a

TABLE II—DETERMINATIONS TO SHOW THE INFLUENCE OF HYDROCHLORIC ACID ON THE SOLUBILITY OF BARIUM SULFATE IN FERRIC CHLORIDE SOLUTION

No.	FeCl ₃ Grams	Na ₂ SO ₄ Grams	HCl (1.19) Cc.	Weight BaSO ₄ Gram
1.....	None	None	0.02	No ppt.
2.....	None	None	0.02	No ppt.
3.....	None	0.0122	0.02	0.0205
4.....	None	0.0122	0.02	0.0204
5.....	14	None	1.00	0.0001
6.....	14	None	1.00	0.0004
7.....	14	0.0122	0.20	Fe pptd.
8.....	14	0.0122	0.40	Fe pptd.
9.....	14	0.0122	0.60	Fe pptd.
10.....	14	0.0122	0.80	Fe pptd.
11.....	14	0.0122	1.00	0.0221 (red)
12.....	14	0.0122	1.20	0.0206 (red)
13.....	14	0.0122	1.40	0.0207 (pink)
14.....	14	0.0122	1.60	0.0204 (gray)
15.....	14	0.0122	1.80	0.0204
16.....	14	0.0122	2.00	0.0210
17.....	14	0.0122	2.20	0.0200
18.....	14	0.0122	2.50	0.0205
19.....	14	0.0122	2.80	0.0209
20.....	14	0.0122	3.10	0.0203
21.....	14	0.0122	3.50	0.0204
22.....	14	0.0122	4.00	0.0210
23.....	14	0.0122	4.50	0.0207
24.....	14	0.0122	5.00	0.0209
25.....	14	0.0122	5.50	0.0203
26.....	14	0.0122	6.00	0.0207
27.....	14	0.0122	6.50	0.0208
28.....	14	0.0122	7.00	0.0207
Average of last 17.....				0.0206
Average deviation.....				0.0002

volume of 120 cc.; precipitations were made hot; solutions stood at the boiling point for an hour, then over night before filtering. Precipitates were washed 3 times with hot dilute hydrochloric acid (10 cc.

1.19 acid in 750 cc. water) and 10 times with hot water.

The barium sulfate equivalent of 0.0122 g. Na_2SO_4 is 0.0200 g. BaSO_4 .

The conclusion seems inevitable that moderate amounts of hydrochloric acid do not appreciably increase the solubility of the barium sulfate in the ferric chloride solution.

The details of the nitric acid and Bamber's method are well known and do not need repetition here. Ordinary directions for the nitric acid method say to add a little sodium salt to hold the SO_3 . What direct evidence this is based upon, the author has not been able to find; the measurements available indicate that ferric sulfate begins to decompose somewhat above 300°C .; 200°C . was the temperature of the laboratory hot plate. No sodium salt was added in any of the analyses.

Bamber's method was carried out with the aid of a vacuum desiccator, an electric muffle and an electric hot plate for evaporating the water extractions of the fusions. During evaporation in the desiccator the temperature was about 95°C ., the gauge at from 10 to 15 in. and a current of air was let in through cotton. In the electric muffle the mass dried in a platinum dish was exposed to a temperature of 900°C . until red hot throughout, which required from 1 to 3 min.

None of the reagents used contained measurable amounts of sulfur in the amount used for analysis.

Blanks run on Bamber's method indicated that check analyses carried through in every detail exactly like a complete determination would average 0.006 per cent sulfur. It is to be noted that such a blank does not determine any impurity in the reagents but rather what has strayed in by accident. The comparatively long evaporations and numerous handlings make the process highly liable to positive error; as already noted, dust bearing 0.0005 g. sulfur would increase results by 0.001 per cent. The laboratory was far from free of dust and fume, as a beam of light will demonstrate in even a reasonably clean place, and during the three days of an analysis it is no wonder that most of the samples ran high by this amount. It is more surprising that some of them checked the nitric acid method almost exactly. As this throws an element of uncertainty on both the analyses and the blanks the only conclusion is that for strictly reliable results the process must be carried out in a place absolutely dust- and fume-free and where the blanks systematically give zero correction. This type of a blank does not register a uniform positive correction but a fortuitous error. Others have usually found that the method gives high results. The conclusion is that Bamber's method, except under the most rigid control, is not as reliable as the nitric acid method.

DETAILS OF CHLORIC ACID METHOD: 5 g. of the well-mixed sample were weighed out into a 400 cc. beaker and the cover-glass placed. The sample was moistened with 2 cc. water and the grains shaken over the bottom so that they would not clump when the acid was added: 40 cc. chloric acid (sp. gr. 1.20) were poured in; solu-

tion took place at once. Enough hydrofluoric acid was added to dissolve the separated silica and immediately the solution was digested with 10 cc. conc. hydrochloric for 2 or 3 min. over a flame. The mixture was then filtered through a 7 cm. paper with suction, and 10 cc. conc. hydrochloric acid were added to the filtrate which was evaporated to small bulk.

The residue on the paper was placed on a little sodium peroxide and sodium carbonate mixture in a nickel or silver crucible, some of the mixture placed above for a cover, and with the crucible cover held down with the tongs the crucible heated in a bare flame. After the flash the melt may be swirled to complete fusion and then poured on metal. If the chloric acid is barium-free the melt may be dissolved in dilute hydrochloric acid and added to the main portion. If the chloric acid contained barium the melt is to be dissolved in water, filtered, acidified, and then added to the main portion.

The united solutions should now contain about the right amount of free acid and if clear may be brought to 100 cc. volume for precipitation of the sulfur as barium sulfate. If the solutions have separated silica they must be filtered before making up to standard volume. To the hot solution 10 cc. of 10 per cent barium chloride solution are added, the beaker is placed to keep just below boiling for an hour, then set aside to cool and filtered the next morning. The barium sulfate is filtered, ignited and weighed as usual.

Sodium fluosilicate may separate on mixing the two solutions or later. This is one of the most insoluble sodium salts and if it appears must be washed out with hot water. On this account as little hydrofluoric acid and sodium salts as possible should be used. The crystals are large and transparent and easily noted if present.

Sulfur present in the chloric acid must be corrected for on the final result.

PRECISION OF RESULTS

A little familiarity with this type of analytical work brings out clearly those sources of error which make up the inequality of the results as recorded in Table III.

TABLE III—AVERAGE RESULTS BY THE THREE METHODS

METHOD: Sample	Lots	NITRIC ACID		Lots	BAMBER'S		Lots	CHLORIC ACID	
		Av. % S	Probable Error		Av. % S	Probable Error		Av. % S	Probable Error
1 Iron...	4	0.008	0.001	3	0.016	0.002	2	0.014	0.002
2 Iron...	4	0.009	0.001	4	0.018	0.001	3	0.014	0.003
3 Steel...	3	0.009	0.002	..	..	..	2	0.015	0.003
4 Iron...	5	0.013	0.001	3	0.021	0.001	2	0.023	0.001
5 Steel...	3	0.018	0.002	5	0.020	0.001	2	0.016	0.001
6 Iron...	7	0.025	0.001	6	0.034	0.002	2	0.038	0.002
7 Iron...	6	0.028	0.002	8	0.041	0.001	4	0.030	0.005
8 Iron...	2	0.030	0.000	5	0.035	0.004	3	0.039	0.004
9 Steel...	4	0.032	0.001	3	0.030	0.002	2	0.030	0.003
10 Iron...	6	0.032	0.002	3	0.042	0.001	3	0.038	0.002
11 Iron...	3	0.038	0.003	3	0.039	0.005	5	0.049	0.002
12 Iron...	4	0.039	0.001	3	0.045	0.002	2	0.043	0.004
13 Iron...	5	0.050	0.003	6	0.059	0.002	3	0.052	0.002
14 Iron...	2	0.061	0.001	5	0.066	0.003	2	0.065	0.002
15 Iron...	6	0.064	0.002	5	0.071	0.003	4	0.063	0.003
16 Iron...	5	0.069	0.003	6	0.076	0.003	2	0.069	0.002
17 Iron...	3	0.077	0.002	2	0.084	0.001	2	0.074	0.002
18 Iron...	5	0.081	0.002	3	0.092	0.002	2	0.080	0.001
19 Iron...	4	0.101	0.002	3	0.103	0.000	2	0.098	0.001
20 Iron...	4	0.117	0.003	3	0.136	0.004	3	0.131	0.003
21 Iron...	7	0.179	0.004	4	0.198	0.004	2	0.186	0.014
22 Iron...	4	0.259	0.004	3	0.267	0.002	2	0.261	0.013

(1) There are slight variations due to the deviations inherent in working with barium sulfate: precipitating in the acid ferric chloride solution, filtering,

washing and igniting. This degree of uncertainty is best indicated in Table II; depending on the total amount of the sulfate weighed the percentage error is greater or less but evidently means a per cent sulfur variation of from 0.001 per cent to 0.002 per cent above or below the true value.

(2) There appear in most of the samples wider fluctuations due to the inhomogeneity of the material; superimposed upon the digressions inherent in the method this often causes a result to deviate several times the average deviation. This difficulty has been continually recorded in the literature and could be further discussed from the preceding results if space allowed. It demands that for any really accurate determination of sulfur enough lots be run to establish the range on the sample at hand. If it were possible to grind so that the entire sample will pass an 80-mesh screen this entire difficulty should vanish.

(3) A source of error comes unexpectedly from laboratory conditions or the liabilities of the somewhat difficult determination that sulfur is. An unnoticed cloud of dust might make a constant error in an entire batch of determinations, for common laboratory dust reeks with sulfur and a quite imperceptible drift of sodium sulfate particles would damage everything exposed. Another source of this type of error lies in holding all the sulfur on solution in nitric acid. Even with great care sulfur may be lost in the fumes. In fact, every method yet proposed for the minutely occurring sulfur in iron or steel has plenty of sources of this sort of error. Bamber's method with its tediousness and many transfers is especially liable; the chloric acid method has the same introduced through the use of hydrofluoric acid and the fusion of the residue. All oxidation check results recorded in the literature bear witness to the correctness of this conclusion.

Composite samples of the barium sulfate precipitates were well mixed and analyzed as follows:

TABLE IV—PERCENTAGES OF IMPURITIES IN BARIUM SULFATE PRECIPITATES

	Chlorine	Ferric Oxide	Silica
Bamber's Method.....	0.14	0.35	0.81
Nitric-Hydrochloric Method.....	0.21	0.79	0.49
Chloric Acid Method.....	0.11	1.64	1.23

Of course the residues from high sulfur samples predominate in such a composite and it gives no indication of individual goodness or badness; the table is interesting as showing the greatest purity for the Bamber residues, as might be expected, but the almost equal purity of the nitric acid precipitates.

SUMMARY

I—A bibliography covering 285 original articles relating to the determination of sulfur in ferrous materials has been compiled and appears below.

II—The methods of sulfur determination have been classified and very briefly discussed.

III—The character of the sample as regards sulfur segregation has been emphasized and illustrated. The fineness of the sample wholly to correct segregation on the material actually used for the analysis should be such that it will pass an 80-mesh screen.

For coarse material precise results can be obtained

only by running a series of analyses which will indicate the limits of the variations.

IV—Bamber's, the Nitric-Hydrochloric and the Chloric Acid methods were tried on some 22 samples ranging from 0.008 to 0.25 per cent sulfur and comprising 238 results.

V—A series to test directly the reliability and precision of the nitric acid method as affected by the solubility of barium sulfate in ferric chloride solution of varying hydrochloric acid content fully substantiates the wide-spread confidence in the method.

VI—Bamber's method is seen to be especially liable to high results due to its length and liability to contamination. Blank check results indicate that if carried out under the best of conditions in a special laboratory the results would almost exactly agree with those by the nitric acid method.

VII—The Chloric Acid method is found to give results usually between those of the first two methods mentioned. The advantage of the method lies in the almost instant and gentle solution of the material and in wholly avoiding the use of nitric acid. The difficulty of the method lies in the accompanying use of hydrofluoric acid which attacks the beakers and may bring a separation of sodium fluosilicate to be dissolved away from the final barium sulfate precipitate. Dehydration of the chlorate solution does not seem to give as good results and lengthens the process. By this method it is possible to have the barium sulfate precipitated in about 20 minutes after the sample is weighed out.

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- 1868—W. F. Gintl. *Z. anal. Chem.*, Vol. 7, page 427. "Über die Bestimmung des Schwefelgehaltes im Roheisen." Dissolves in ferric chloride, oxidizes residue with an alkaline fusion, weighs as BaSO_4 .
- 1869—D. Forbes. *Chem. News*, Vol. 16, page 105. "Analysis of Blister Steel." Evolution method; H_2S is absorbed by Zn in ZnCl_2 , then oxidized to BaSO_4 .
- 1869—Lefort. *Chem. News*, Vol. 19, page 132. "Action of Aqua Regia on Sulfur." States best mixture for oxidizing elemental sulfur.
- 1869—F. H. Storer. *Am. J. Sci.*, Vol. 48, page 190. "On the Nitric Acid and Chlorate of Potassium as an Oxidizing Mixture." Precipitates in a tartrate solution; washes with ammon. acetate to purify BaSO_4 .
- 1870—H. B. Hamilton. *Chem. News*, Vol. 21, page 147. "Determination of Sulfur in Irons." A modified Fresenius evolution method; 6 results are given; the checks are poor.
- 1870—L. Koninck. *Rev. Univ. Mines*, Vol. 28, page 402. "Dosage du Soufre dans la fonte: Procédés nouveaux par L. De Koninck." Evolution method with absorption in AgNO_3 , oxidizes with Br, weighs as BaSO_4 .
- 1870—E. Richters. *Dingler's polytech. J.*, Vol. 197, page 168. "Zur Bestimmung des Schwefels, Phosphors und Siliciums in Roheisen." Of slight import.
- 1871—A. H. Elliott. *Chem. News*, Vol. 23, pages 61 and 143. "Estimation of Sulfur in Cast-Iron." Evolution method; absorbs H_2S in NaOH , iodine titer.
- 1871—Glendinning and Edgar. *Chem. News*, Vol. 24, pages 140 and 220; also Vol. 27, page 13. "On the Estimation of Sulfur by Barium." Affirms that precision can be obtained by determining S as BaSO_4 .
- 1871—K. Meinecke. *Z. anal. Chem.*, Vol. 10, page 280. "Bestimmung des Phosphor und Schwefel-Gehaltes in Eisen." Uses copper-sodium chloride to effect solution; oxidizes and weighs as BaSO_4 .
- 1871—Teschemacher and Smith. *Chem. News*, Vol. 24, pages 61 and 66. "On the Estimation of Sulfur by Barium." Disparages oxidation methods.
- 1872—A. H. Elliott. *Chem. News*, Vol. 15, page 35. "A. H. Elliott's Method for Sulfur in Cast-Iron." Note says evolution method is easier than chlorine or double chloride methods and admits low combined carbon in samples tried.
- 1872—T. J. Morrell. *American Chemist*, Vol. 3, page 180. "Estimation of Sulfur in Iron and Steel." Evolution method; weighs as CdS .
- 1872—S. Peters. *Chem. News*, Vol. 25, page 11. "Sulfur Estimation in Cast-Iron by Mr. A. H. Elliott's Method." With white iron sulfide left in residue.
- 1873—M. Koppmeyer. *Dingler's polytech.*, Vol. 210, page 184. "Bestimmung des Schwefels im Roheisen, Schmiedeeisen und Stahl." Usual iodine titration method.
- 1873—C. H. Piesse. *Chem. News*, Vol. 28, pages 248 and 276. "On the Estimation of Sulfur in Pig-Irons, Etc." Uses aqua regia oxidation method with standard details.
- 1873—W. Mattieu. *Chem. News*, Vol. 28, page 266. "The Estimation of Sulfur in Pig Irons." Says method of Piesse is a very old one; discusses evolution and oxidation methods.
- 1873—A. Sauer. *Z. anal. Chem.*, Vol. 12, pages 32 and 178. "Eine Schwefelbestimmungsmethode von allgemeiner Anwendbarkeit." Burns the substance in oxygen but does not mention trying ferrous materials.
- 1874—Alfred H. Allen. *Chem. News*, Vol. 29, page 91. "Estimation of Silicon and Graphite in Pig-Irons." Criticizes Piesse's method; wants to precipitate BaSO_4 in almost neutral solution and let stand from 24 to 36 hours.
- 1874—Th. M. Drown. *Trans. Am. Inst. Mining Eng.*, Vol. 2, page 224. "Determination of Sulfur in Pig-Iron and Steel." Absorbs H_2S in KMnO_4 ; one result given.
- 1874—R. Fresenius. *Z. anal. Chem.*, Vol. 13, page 37. "Zur Bestimmung des Schwefels im Roheisen, Stahl, Etc." Evolution in H_2 atmosphere.
- 1874—C. H. Piesse. *Chem. News*, Vol. 29, page 112. "Estimation of Carbon and Silicon in Pig-Irons." Neutralizing solution before precipitation of BaSO_4 is of no practical use.
- 1875—Boussingault. *Ann. chim. phys.* [5], Vol. 5, page 145. "Études sur la transformation du fer en acier par la cementation." Several pages on evolution method for sulfur; prefers to collect in AgNO_3 , weighing equivalent Ag.
- 1875—F. Muck. *Z. anal. Chem.*, Vol. 14, page 16. "Zu A. Sauer's Schwefelbestimmungsmethode." Finds SO_2 always deposited through apparatus.
- 1876—R. Wagner. *Dingler's polytech. J.*, Vol. 219, page 544. "Ueber die Verwendbarkeit des Broms in der Hydrometallurgie der Probirkunst und der chemischen Technologie." A review; says Berthier first used bromine for iron analysis in 1833.
- 1877—Delachanal et Mermet. *Ann. chim. phys.*, Vol. 12, page 88. "Méthodes d'analyse complète des sulfures et..." Oxidizes sulfur in many substances with use of Br in KOH .
- 1877—J. E. Hibsch. *Dingler's polytech. J.*, Vol. 225, page 61. "Ueber einige Methoden zur Bestimmung des Schwefels im Roheisen." Brief review with few poorly comparative figures.
- 1878—Fahlberg and Iles. *Ber.*, Vol. 11, page 1187. "Eine neue Methode zur quantitativen Bestimmung von Schwefel." Alkaline fusion with oxidation by Br; applies to all organic and sulfide substances.
- 1879—Delachanal et Mermet. *Bull. soc. chim. Paris*, Vol. 32, page 50. "Reclamation d'après d'une nouvelle méthode de dosage du soufre." Refers to work published two years earlier.
- 1879—A. Rollet. *Dingler's polytech. J.*, Vol. 233, page 124. "Bestimmung des Schwefels in den Producten der Eisen-Industrie, den Erzen und den Brennmaterialien." Evolution method in current of H_2 and CO ; weighs as Ag_2S .
- 1880—R. Fresenius. *Z. anal. Chem.*, Vol. 19, page 53. "Zur Bestimmung des Schwefelgehaltes der Schwefelkies." Studies the solubility and purity conditions of BaSO_4 .
- 1881—T. O'C. Sloane. *J. Am. Chem. Soc.*, Vol. 3, page 37. "Note on the Precipitation and Purification of Barium Sulfate." States his ideas on conditions for accurate results.
- 1882—George Craig. *Chem. News*, Vol. 46, pages 199 and 272. "Estimation of Sulfur in Iron and Steel." Evolution method with absorption in H_2O_2 and weigh as BaSO_4 ; four results. Refutes Rocholl.
- 1882—H. Rocholl. *Chem. News*, Vol. 46, page 236. "Estimation of Sulfur in Pig Iron." Evolution method always leaves sulfur in residue; this must be oxidized to get full amount.
- 1882—A. Tamm. *Chem. Centr.*, page 766; through *J. Chem. Soc. London*, Vol. 44, page 511. Review of evolution methods.
- 1882—Ziegler. *J. Iron Steel Inst.*, page 384. Adds AgNO_3 after the BaCl_2 to completely bring down BaSO_4 ; AgCl removed with NH_4OH .
- 1883—Classen and Bauer. *Ber.*, Vol. 1, page 1061. "Ueber die Anwendbarkeit des Wasserstoffsperoxyds in der analytischen Chemie." Uses H_2O_2 and Br to oxidize H_2S to H_2SO_4 .
- 1884—Thomas Bayley's Book, "The Assay and Analysis of Iron and Steel, Iron Ores and Fuel." E. & F. N. Spon, London. Oxidation method with fusion purification of BaSO_4 .
- 1884—A. Brand. *Berg. u. Hütt. Zeit.*, Vol. 43, page 346. "Verfahren zur Analyse von Stahl." One paragraph on evolution method.
- 1884—Perillon. *Bull. soc. ind. min.*, Vol. 13, page 103. "Dosage rapide du Carbone, du phosphore, Etc." Boussingault's method, KSCN .
- 1884—Scheurer-Kestener. *Compt. rend.*, Vol. 99, page 876. "Réaction de l'oxyde ferrique à haute température sur quelques sulfates." Loss of SO_3 on heating ferric oxide with sulfates.
- 1884—M. Troilius. *Trans. Am. Inst. Mining Eng.*, Vol. 12, page 507. "Sulfur Determination in Steel." Evolution method using Br to BaSO_4 .
- 1885—N. Von Klobulow. *Ber.*, Vol. 18, page 1861. "Ueber eine neue Methode zur quantitativen Bestimmung des Schwefels." A zinc-evolution method for sulfur in anything.
- 1885—Osmond. *Bull. soc. chim. Paris*, Vol. 43, page 70. "Sur l'absorption et le dosage de petites quantités d'hydrogène sulfuré dans les mélanges gazeux." Silver salts give sharper results than lead or copper.
- 1885—J. Peters. *Bull. soc. chim. Paris*, Vol. 44, page 16. "Dosage du soufre dans les aciers, fers et fontes." Evolution, absorbs in KMnO_4 .
- 1885—Reinhardt. *Stahl u. Eisen*, Vol. 5, page 550. "Ueber Schwefelbestimmungs-Apparate." Notes elemental sulfur when using Br solution.
- 1885—L. Rinman. *Jern-Kont. Annaler*, Vol. 40, page 362. "Svafvelproff på tackjern." Anneals white iron in crucible before colorimetric detn.
- 1886—W. F. Brugman. *School Mines Quart.*, Vol. 8, page 74. "Influence of Copper on the Estimation of Sulfur." Copper without influence.
- 1886—Gustav Möller. *Berg. u. Hütt. Zeit.*, Vol. 45, page 198. "Ueber die Eggertz'sche Bestimmung des Schwefels im Eisen." Disparages it.
- 1886—V. Eggertz. *Berg. u. Hütt. Zeit.*, Vol. 45, page 545. "Ueber die Colorimetric Bestimmung des Schwefels im Eisen." Uses metal foil.
- 1886—Springer. *Berg. u. Hütt. Zeit.*, Vol. 45, page 471. "Verfahren zur Analyse von Eisen und Stahl." Evolution method into Br with CO_2 .
- 1886—J. Wiborgh. *Jern-Kont. Annaler*, Vol. 41, page 105. "Nytt Kolorimetriskt svafvelproff för jern." Also in *Stahl und Eisen*, Vol. 6, page 230 with cut and color chart. The famous color method with 27 check results.
- 1887—Föhr. *Oesterr. Chem.-Tech.-Zeit.*, Vol. 5, page 105; through *Chem. Zentr.*, 1887, 871. Evolution method, H_2S into ammoniacal zinc solution, reacts with ferric sulfate and KMnO_4 titer.
- 1887—J. J. Morgan. *Chem. News*, Vol. 36, page 82. From Industrial Review by Morgan. "Rapid Methods for the Determination of Silicon, Sulfur and Manganese in Iron and Steel." Refinement of Parry's method; evolution method with color comparison in lead acetate tubes.
- 1887—B. Platz. *Stahl u. Eisen*, Vol. 7, page 256. "Zur Bestimmung des Schwefels im Eisen." Oxidation method, precautions for pure BaSO_4 .
- 1887—A. Tamm. *Jern-Kont. Annaler*, Vol. 42, page 4. "Nagra meddelander rörande kemisk profning af jern och jernmalin." Review of methods; study of BaSO_4 purification.
- 1888—J. O. Arnold and Henry J. Hardy. *Chem. News*, Vol. 58, pages 41 and 71. "New Methods for the Estimation of Sulfur in Steel and Steel-Making Iron." "Estimation of Sulfur in Iron and Steel." Review of methods and claim new accuracy for evolution-colorimetric method, using lead acetate in tubes. Maintain against Morgan.
- 1888—V. Gröndahl. *Oesterr. Chem.-Tech.-Zeit.*, Vol. 6, page 621; through *Jahresbericht*, 1888, 2529. Evolution method, H_2S into H_2O_2 , weigh as BaSO_4 .
- 1888—L. L. de Koninck. *Z. angew. Chem.*, Vol. 1, page 311. "Bestimmung des Schwefels im Eisen und in den von Salz und Schwefelsäure zersetzbaren Schwefelmetallen." Uses $\text{Hg}(\text{NO}_3)_2$ and NH_4Cl .
- 1888—M. Lucion. *Chem. Ztg.*, Vol. 12, page 427. "Ueber die Fällung von Baryumsulfat in bromhaltigen Flüssigkeiten." Bromine in solution is without influence on the solubility of BaSO_4 .
- 1888—J. Leutscher. *Iron Age*, Vol. 41, page 325. "The Use of Centrifugal Machines in the Iron and Steel Laboratory." Measures the PbS ppt.
- 1888—C. Meinecke. *Z. angew. Chem.*, Vol. 1, page 376. "Ueber die Bestimmung des Schwefels im Eisen." 7 samples show weakness of evolution method; then 7 by his old copper-sodium chloride method give correct results.
- 1888—J. J. Morgan. *Chem. News*, Vol. 58, page 59. Call Arnold and Hardy's new method only modification of Parry's.
- 1888—J. J. Morgan. *Chem. News*, Vol. 58, page 63. "On the Determination of Sulfur in Iron and Steel." General review and discussion of all methods.
- 1888—Prost. *Bull. acad. roy. belg.*, Vol. 16, page 216. "Étude de l'action de l'acide chlorhydrique sur la fonte." Organic sulfur compounds are evolved and in residue.
- 1888—W. Thörner. *Z. angew. Chem.*, Vol. 1, page 487. "Ueber einen verbesserten Zersetzungs- und Absorptions-Apparat." Cuts and details.
- 1888—B. W. Winder. *Chem. News*, Vol. 58, page 95. "Estimation of Sulfur in Iron and Steel." Says Morgan's methods are all old and well known.
- 1889—Jannasch and Richards. *J. prakt. Chem.*, N. S., Vol. 39, page 321. "Ueber die Bestimmung der Schwefels, ure bei Gegenwart von Eisen." Works with salts; finds only fusion method accurate.
- 1889—Marsh. *J. Anal. Appl. Chem.*, Vol. 3, page 164. "The Reduction of Barium Sulfate to Barium Sulfide on Ignition with Filter-Paper." Reduction is found in the 30 samples investigated.
- 1889—B. Platz. *Stahl u. Eisen*, Vol. 9, page 405. "Zur Bestimmung des Schwefels in Eisen." Finds no H_2S lost when diss. in HNO_3 ; results on 5 samples.
- 1889—M. A. von Reis. *Stahl u. Eisen*, Vol. 8, page 827. "Zur Bestimmung des Phosphors und Schwefels im Eisen." Sinters fine metal with magnesia and soda; results on 18 samples.
- 1889—M. A. von Reis. *Stahl u. Eisen*, Vol. 9, page 497. "Zur Bestimmung des Schwefels im Eisen." Questions accuracy of dissolving in HNO_3 .
- 1889—E. F. Smith. *J. Franklin Inst.*, Vol. 127, page 313. "Oxidation by Means of the Electric Current." Electrical oxidation of sulfur to Na_2SO_4 in alk. fusion.
- 1889—A. Vosmaer. *Chem. Ztg.*, Vol. 13, page 695. "Ueber die Wiborgh'sche colorimetrische Schwefelbestimmungsmethode." Presents certain refinements.
- 1890—L. Archbutt. *J. Soc. Chem. Ind.*, Vol. 9, page 25. "The

- Determination of Sulfur in Iron and Steel." *Oxidation method; tests solubility of BaSO₄.*
- 1890—L. Blum. *Z. anal. Chem.*, Vol. 29, page 138. "Zur Bestimmung des Schwefels im Eisen." *Fears solubility of BaSO₄ in HBr.*
- 1890—J. B. Cohn. *J. Soc. Chem. Ind.*, Vol. 9, page 16. "Wiborgh's Method for the Analysis of Sulfur in Iron and Steel." *Describes the method.*
- 1890—C. Reinhardt. *Stahl u. Eisen*, Vol. 10, page 430. "Schnelle gewichtsanalytische Schwefelbestimmung in Stahl und Roheisen." *Evolution Br-oxidation method with known sulfur in the solution to filter small amounts easier.*
- 1890—W. Thörner. *Chem. Ztg.*, Vol. 14, page 1655. "Mittheilungen aus der Laboratoriumspraxis." *Refinements of evolution process.*
- 1891—J. M. Camp. *J. Anal. Appl. Chem.*, Vol. 5, page 409. "Absorption Apparatus for Sulfur Determination." *Tube filled with beads and bromine water.*
- 1891—G. Hattensauer. *Chem. Ztg.*, Vol. 15, page 521. "Zur Schwefelbestimmung in Eisen und Stahl." *Evolution method and solution in cupric chloride give same results; 7 samples compared.*
- 1891—Reis und Wigert. *Stahl u. Eisen*, Vol. 11, page 480. "Zur Bestimmung von Schwefel im Eisen." *Evolution method with oxidation of H₂S and its precipitation with barium nitrate given as a quick method.*
- 1891—A. J. Rossi. *Stahl u. Eisen*, Vol. 11, page 927. "Bestimmung von Schwefel." *Combination of evolution and Br-oxidation methods.*
- 1891—F. P. Treadwell. *Ber.*, Vol. 24, page 1937. "Beitrag zur quantitativen Bestimmung des Schwefels." *Changes sulfur to FeS and uses evolution method.*
- 1891—J. M. Wilson. *J. Anal. Appl. Chem.*, Vol. 5, page 439. "A Method of Standardizing Iodine Solution for the Determination of Sulfur in Steel and Pig Iron." *Standardizes against sample of known sulfur content.*
- 1892—H. C. Babbitt. *J. Anal. Appl. Chem.*, Vol. 6, page 301. "Wiborgh's Colorimetric Sulfur Determination." *Describes the process.*
- 1892—L. Blum. *Z. anal. Chem.*, Vol. 31, page 290. "Absorptions-apparat zur Bestimmung des Schwefels im Eisen." *Improved apparatus.*
- 1892—Lee S. Clymer. *J. Anal. Appl. Chem.*, Vol. 6, page 318. "Sulfur Determinations by Different Methods." *Startling results by international analysis and by different methods.*
- 1892—A. T. Eastwick. *J. Anal. Appl. Chem.*, Vol. 6, page 246. "The Determination of Sulfur in Iron and Steel." *Concerns iodine-evolution method.*
- 1892—J. van Leeuwen. *Chem. Centr.*, Vol. 63 [2], page 757. From R. P. B., Vol. 11, page 103. "Einfluss des Schwefels des Steinkohlengases auf die Bestimmung des Schwefels durch Schmelzung." *Uses a spirit flame.*
- 1892—J. van Leeuwen. *Rec. trav. chim.*, Vol. 11, page 103. "L'influence du soufre du gaz de houille sur le dosage du soufre par fusion." *Use alcohol or benzene flame.*
- 1892—H. L. Payne. *J. Anal. Appl. Chem.*, Vol. 6, page 481. "Standard Iodine Solution: A Method for Its Preparation." *Iodine freed by permanganate.*
- 1892—M. Ripper. *Z. anorg. Chem.*, Vol. 2, page 36. "Beiträge zur Gewichtsanalyse der Schwefelsäure." *A critical paper on BaSO₄ with some results.*
- 1892—A. Schneider. *Z. physik. Chem.*, Vol. 10, page 423. "Ueber einen Fall der festen Lösung." *Finds a rather constant per cent of iron in BaSO₄ ppt.*
- 1892—F. P. Treadwell. *Ber.*, Vol. 25, page 2377. "Beitrag zur Schwefelbestimmung II." *As above and uses H₂O₂ or iodine titer.*
- 1892—F. H. Williams. *Eng. Soc. West. Penn.*, Vol. 8, page 328. "Note on the Use of Hot Acid in the Evolution of Sulfur as H₂S from Pig-Iron." *A few results on hot, cold, concentrated and dilute acid.*
- 1893—F. L. Crobaugh. *J. Anal. Appl. Chem.*, Vol. 7, page 280. "Cadmium Chloride as an Absorbent of Hydrogen Sulfid." *States minimum quantity necessary.*
- 1893—H. A. Hooper. *Chem. News*, Vol. 68, page 191. "A New Method for the Rapid Estimation of Sulfur in Steels, Pig-Irons, Etc." *Evolution method, titrates with standard lead solution.*
- 1893—E. M. Stahl u. Eisen, Vol. 13, page 686. "Zur Schwefelbestimmung. Special apparatus for evolution method.
- 1893—J. K. Mackenzie. *J. Anal. Appl. Chem.*, Vol. 7, page 134. "Absorption Bulb for Sulfur Determinations." *Convenient form with stopcock.*
- 1893—Parry and Morgan. *Chem. News*, Vol. 67, page 247. From "Industries." "The Analysis of Iron and Steel." *Aqua regia oxidation method.*
- 1893—W. Schindler. *Z. angew. Chem.*, Vol. 6, page 11. "Beitrag zur Schwefelbestimmung im Eisen nach der Schwefelwasserstoffmethode." *Concentrated HCl gives all sulfur by either Br or H₂O₂ oxidation to H₂SO₄.*
- 1893—L. Schneider. *Oesterr. Z. Berg. Hüttenw.*, Vol. 41, page 365. "Beiträge zur Chemischen Untersuchung des Stahles." *Evolution method with absorption in KMnO₄.*
- 1894—H. K. Bamber. *J. Iron Steel Inst.*, Vol. 45 [1], page 319. "On the Analysis of Steel." *States the fusion method in detail with results on 6 samples.*
- 1894—T. S. Gladding. *J. Am. Chem. Soc.*, Vol. 16, page 398. "On the Estimation of Sulfur in Pyrites." *A small pertinent research.*
- 1894—F. Johnson. *Chem. News*, Vol. 70, page 212. "The Estimation of Sulfur in Pyrites." *Adds H₂NaPO₄ to reduce iron and rid of nitrates.*
- 1894—M. A. von Reis. *Stahl u. Eisen*, Vol. 14, page 963. "Zur Bestimmung von Schwefel im Eisen." *Details for accuracy in evolution method; oxidizes with H₂O₂.*
- 1894—J. F. Sleeper. *Chem. News*, Vol. 69, page 63. "On the Precipitation of Barium Sulfate in the Presence of Silica, and the Decomposing Action of Hydrofluoric Acid on the Former." *Interesting results with analytical figures.*
- 1894—Spüller and Kahlmann. *Chem. Ztg.*, Vol. 18, page 2040. "Bestimmung des Schwefels in Stahl und Eisen." *Evolution method absorbing in Na₂O₂; uses current of N₂; weighs as BaSO₄.*
- 1895—J. O. Arnold's Book: "Steel Works Analysis." Pub. by Whitaker & Co., London. Pages 96 to 110 on sulfur determination.
- 1895—L. Campredon. *Compt. rend.*, Vol. 120, page 1051. "Dosage du soufre dans les fontes, les aciers et les fers." *Iodine evolution method using CO₂ and H₂.*
- 1895—A. Carnot. *Rev. Univ. Mines*, Vol. 8, page 357. "Methodes d'analyse des fontes, des fers et les aciers." *A lengthy review.*
- 1895—A. Carnot's Book: "Methodes d'Analyse des Fontes, des Fers & des Aciers." Pub. by Dunod & Vicq., Paris. Pages 82 to 96 on sulfur.
- 1895—A. Forestier. *Bull. soc. chim. Paris*, Vol. 13, page 586. "Essai des aciers, fer et fontes par l'analyse chimique." *Brief review.*
- 1895—H. F. J. von Jorstorff's Book: "Fortschritte im Eisenhütten-Laboratorium." Pub. by A. Felix, Leipzig. Pages 115 to 142 about sulfur.
- 1895—L. L. DeKoninck. *Chem. Ztg.*, Vol. 19, page 502. "Vorschlag zur Bestimmung von Schwefel in Eisensorten." *Evolution method using SnCl₄.*
- 1895—G. Lunge. *J. Am. Chem. Soc.*, Vol. 17, page 181. "On the Estimation of Sulfur in Pyrites." *Refutes Gladding's variations with several analyses according to his own method.*
- 1895—G. Lunge. *Z. angew. Chem.*, Vol. 8, page 69. "Ueber die Bestimmung des Schwefels im Schwefelkies." *Same as in J. Am. Chem. Soc.*
- 1895—F. C. Phillips. *J. Am. Chem. Soc.*, Vol. 17, page 891. "The Evolution Method for the Determination of Sulfur in White Cast-Iron." *Critical study of evolution method; finds organic sulfur compounds. Many results given; an important contribution.*
- 1895—E. J. Read. *Chem. News*, Vol. 72, page 299. "Apparatus for Estimation of Sulfur in Iron." *Ueber die Einschliessung von Baryumchlorid durch Baryumsulfat." Study of BaSO₄ pptn.*
- 1896—George Auchy. *J. Am. Chem. Soc.*, Vol. 18, page 406. "Drown's Method of Determining Sulfur in Pig Iron." *Evolution with absorption in KMnO₄; mainly study of effect of oxalic acid on BaSO₄.*
- 1896—G. G. Boucher. *Chem. News*, Vol. 74, page 76. "Estimation of Sulfur in Cast-Iron or Steel." *Recommends copper ammonium chloride method for accuracy; essentially Meinecke's method. Results on 6 samples.*
- 1896—C. W. Foulk. *J. Am. Chem. Soc.*, Vol. 18, page 793. "The Effect of an Excess of Reagent in the Precipitation of Barium Sulfate." *An excellent study with the now well-known conclusions.*
- 1896—Fresenius and Hintz. *Z. anal. Chem.*, Vol. 35, page 170. "Ueber eigenthümliche Löslichkeitsverhältnisse des schwefelsauren Baryts." *13 pages on the solubility of BaSO₄ in water and salt solutions.*
- 1896—T. S. Gladding. *J. Am. Chem. Soc.*, Vol. 18, page 446. "On the Estimation of Sulfur in Pyrites." *Holds for slow addition of precipitant.*
- 1896—M. Lucas. *Bull. soc. chim. Paris*, Vol. 17, page 144. "Les Methodes de dosage du Phosphore et du soufre, dans le fer, l'acier et la fonte." *Evolution method with red-hot tube. Table of results—mostly as published by others.*
- 1896—M. Lucas. *Bull. soc. chim. Paris*, Vol. 17, page 150. "Application de la méthode de dosage colorimétrique du plomb au dosage du soufre dans le fer, l'acier et la fonte." *Absorbs H₂S in alkaline lead sol. and makes precise color estimation by purifications.*
- 1896—F. A. Matthewman. *J. West. Scot. Iron Steel Inst.*, Vol. 3, page 1. From *J. Iron Steel Inst.*, Vol. 49 [1], page 537. *Reported of some importance; original article not available.*
- 1896—J. J. Morgan. *Chem. News*, Vol. 72, page 257. "Estimation of Sulfur in Cast-Iron or Steel." *Discusses Boucher's method and refers it to C. Meinecke, 1888.*
- 1896—F. C. Phillips. *J. Am. Chem. Soc.*, Vol. 18, page 1079. "The Determination of Sulfur in Cast Iron." *Direct oxidation method; nitrate and heat.*
- 1896—Wilhelm Schulte. *Stahl u. Eisen*, Vol. 16, page 865. "Eine Neue Methode zur Bestimmung des Schwefels im Eisen." *Develops the evolution method, using Cd(CaH₃O₂)₂, CuSO₄, CuS and weighing as CuO.*
- 1896—H. Wedding's Book: "Handbuch der Eisenhüttenkunde." Pub. by F. Vieweg & Sohn, Braunschweig. Gives 10 methods.
- 1897—A. A. Blair. *J. Am. Chem. Soc.*, Vol. 19, page 114. "The Determination of Sulfur in Pig Iron." *Review Bamber's method in detail; refers to work of Phillips.*
- 1897—G. G. Boucher. *Chem. News*, Vol. 75, page 121. "Volumetric Estimation of Sulfur in Iron, Steel and Sulfides of Iron." *Evolution-titration method, using FeCl₃ and K₂Cr₂O₇; 8 results.*
- 1897—Louis Campredon. *Stahl u. Eisen*, Vol. 17, page 486. "Bestimmung des Schwefels im Eisen." *Confirms necessity of heating gases in evolution method; 1 table.*
- 1897—Carnot and Goutal. *Compt. rend.*, Vol. 125, page 75. "Sur l'emploi des sels cuivriques pour préparer le dosage de divers éléments dans les fontes et les aciers." *Dissolves in Cu-K-chloride solution and oxidizes residue with bromine.*
- 1897—Carnot and Goutal. *Ann. chim. anal.*, Vol. 2, page 301. "Sur l'emploi des sels cuivriques pour préparer le dosage de divers éléments dans les fontes et les aciers." *See above; credits Berzelius with origin of dissolving iron in cupric chloride.*
- 1897—C. B. Dudley. *J. Am. Chem. Soc.*, Vol. 19, page 93. "Some Present Possibilities in the Analysis of Iron and Steel." *Review. Evolution method hazardous, oxidation method slow. Rate of output stated.*
- 1897—O. Herting. *Chem. Ztg.*, Vol. 21, page 87. "Beitrag zur Bestimmung des Schwefels in Eisensorten." *Evolution-iodine method; results on 4 samples.*
- 1897—E. S. Johnson. *J. Am. Chem. Soc.*, Vol. 19, page 288. "Some Apparatus for the Technical Analytical Laboratory." *Stand with burners to hold flasks and absorption tubes for evolution method, using hydrogen.*
- 1897—E. K. Landis. *J. Am. Chem. Soc.*, Vol. 19, page 261. "Standard Iodine Solution for Sulfur Determinations." *Reactions and calculations.*
- 1897—F. Marboutin. *Mon. sci.*, Vol. 50, page 644. "Sur le dosage de l'acide sulfurique. Méthode en poids et méthodes volumétriques." *Mainly titration methods for water analysis.*
- 1897—R. K. Meade. *J. Am. Chem. Soc.*, Vol. 19, page 581. "A New Apparatus for Sulfur Determinations in Iron and Steel and a Useful Form of Wash-Bottle." *Stand to hold evolution flask and separatory funnels for absorption.*
- 1897—Wilhelm Schulte. *Stahl u. Eisen*, Vol. 17, page 489. "Bestimmung des Schwefels im Eisen." *Confirms necessity of passing evolution gases through hot tube; 2 tables of results.*
- 1898—Eng. Soc. West. Penn. Book: "Methods for the Analysis of Ores, Pig Iron and Steel of the Pittsburgh Region." Chem. Pub. Co., Easton, Pa. Various company methods; uncritical.
- 1898—E. Franke. *Stahl u. Eisen*, Vol. 18, page 326. "Zur Bestimmung des Schwefels in Eisen." *A study of modifications of evolution method. 27 samples are run by 5 different methods; remarkable uniformity. Schulte's method best of all.*
- 1898—J. T. Chem. News, Vol. 78, page 294. "Blank Tests." *Gets blank by deducting weight of larger from twice weight of half sample.*
- 1899—Aulich. *Stahl u. Eisen*, Vol. 19, page 878. "Schwefel in Eisenerzen und Eisenhüttenzeugnissen." *Review of oxidation methods.*
- 1899—F. L. Crobaugh. *Iron Trade Review*, Vol. 32, No. 27, page 12. "Methods for the Iron Laboratory—IV, Sulfur." *Evolution method; starts with cold dilute acid; CdCl₂ and iodine titration.*
- 1899—O. Herting. *Chem. Ztg.*, Vol. 23, page 768. "Die brauchbaren Methoden zur Bestimmung des Schwefels im Eisen." *A rather brief review.*
- 1899—Kuster and Thiel. *Z. anorg. Chem.*, Vol. 19, page 97, 1900; Vol. 25, page 319. "Ueber die Bestimmung der Schwefelsäure bei Gegenwart von Eisen." *Figures show that oxalic and tartaric acids keep iron from BaSO₄.*
- 1899—C. Meinecke. *Z. anal. Chem.*, Vol. 38, page 209. "Ueber die Bestimmung der Schwefelsäure, mit besonderer Berücksichtigung der Bestimmung des Schwefels in Eisenerzen und Eisenhüttenprodukten." *Oxidation method; reduces Fe" with zinc and gets results identical with hod.*

- 1899—M. J. Moore. *J. Am. Chem. Soc.*, Vol. 21, page 972. "Notes on the Determination of Sulfur in Pig Iron." *Results depend on cooling of metal.*
- 1899—J. Thill. *Z. anal. Chem.*, Vol. 38, page 342. "Die massanalytische Bestimmung des Schwefels in Roheisen, Stahl u. s. w. durch, arsenige Säure." *Evolution method with arsenite-iodine titration.*
- 1900—B. Blount. *Analyst*, Vol. 25, page 141. "The Determination of Carbon and Sulfur in Steel." *Not possible by direct combustion.*
- 1900—O. N. Heidenreich. *Z. anorg. Chem.*, Vol. 20, page 233. "Ueber die Bestimmung des Schwefels in Kies bei Gegenwart von Eisen." *Reduces before precipitating with BaCl₂; results on 1 sample.*
- 1900—A. Ledebur's Book: "Leitfaden für Eisenhütten-Laboratorien." 5th edition. F. Vieweg & Sohn, Braunschweig.
- 1900—Adolf Riemer. *Stahl u. Eisen*, Vol. 19, page 1064. "Bestimmung des Schwefels in Roh- und Flusseisen." *Disparages Wiborgh's and expounds iodine method.*
- 1901—U. Antony. *Gazz. chim. ital.*, Vol. 31 [ii], page 274. "Determinazione dello zolfo e del fosforo nei prodotti siderurgici." *Alkaline fusion of the fine powder.*
- 1901—George Auchy. *J. Am. Chem. Soc.*, Vol. 23, page 147. "Determination of Sulfur in Wrought Iron and Steel." *Evolution method with constant positive correction; 60 results.*
- 1901—Blair and Shimer. *Trans. Am. Inst. Mining Eng.*, Vol. 31, page 748. "A Crystalline Sulfide in Pig-Iron." *Finds an insoluble C-Fe-Ti-S compd.*
- 1901—A. Classen's Book: "Ausgewählte Methoden der Analytischen Chemie." Pub. by F. Vieweg & Sohn, Braunschweig. 10 pages on sulfur determination.
- 1901—W. G. Lindsay. *School Mines Quart.*, Vol. 23, page 24. "On a Colorimetric Method for the Estimation of Sulfur in Pig Iron." *Forms methylene blue; results on 3 samples.*
- 1901—Noyes and Helmar. *J. Am. Chem. Soc.*, Vol. 23, page 675. "The Determination of Sulfur in Iron and Steel." *Recommends bromine or nitric acid-chlorate-bromide solution with pptn. of iron before adding BaCl₂. Results on 7 samples; suggest constant correction.*
- 1902—Felix Bischoff. "Beiträge zu der Analyse des Eisens." *Stahl u. Eisen*, Vol. 22, page 719. *States allowable deviations in individual results. Ignores unequal distribution.*
- 1902—Felix Bischoff. *Stahl u. Eisen*, Vol. 22, page 754. "Beiträge zu der Analyse des Eisens." *Claims CuS unaffected by evolution method; discusses method and modifications.*
- 1902—Felix Bischoff. *Stahl u. Eisen*, Vol. 22, page 1136. "Beiträge zu der Analyse des Eisens." *Refutes Naske with results on 9 samples.*
- 1902—Brearley and Ibbotson's Book: "The Analysis of Steel-Works Materials." Longmans, Green & Co. Excellent chapter and essay on sulfur. Summarizes important contributions. 150 references in bibliography, mostly from "Chem. News" and "J. Iron and Steel Inst." Nothing new but advice.
- 1902—Geo. T. Dougherty. *Iron Age*, Vol. 69, page 14. "Notes on Iron Analysis." *Improved annealing; results on 6 samples.*
- 1902—T. Naske. *Stahl u. Eisen*, Vol. 22, page 333. "Colorimetrische Methode zu Bestimmung des Schwefels im Roheisen." *Enlarges on errors of color and evolution methods.*
- 1902—T. Naske. *Stahl u. Eisen*, Vol. 22, page 1134. "Beiträge zu der Analyse des Eisens." *Asserts hydrides of As, P and Si spoil Bischoff's evolution method.*
- 1902—J. V. R. Stehman. *J. Am. Chem. Soc.*, Vol. 24, page 644. "The Application of Eschka's Method to Pig Irons." *Good results with finely ground sample.*
- 1902—Walters and Miller. *Eng. Soc. West. Penn.*, Vol. 18, page 83. "An Accurate Estimation of Sulfur in Iron by the Evolution Method." *Anneals samples before evolution method; results on 19 samples.*
- 1902—A. Wencelius's Book: "Methods d'Analyse des Laboratoires d'Acieries Thomas." Beranger, Paris. *Schulze's method on page 48.*
- 1903—W. E. Dickson. *Iron Trade Review*, Vol. 36, page 61. "Loss of Sulfur in Borings of Cast Iron." *Results on 7 samples; steel no loss.*
- 1903—H. E. Field. *J. Am. Foundrymen's Assoc.*, Vol. 11, page 129. "Standard Methods for Analyzing Iron." *States numerous minute details for both evolution and oxidation processes.*
- 1903—W. G. Ireland. *Iron Trade Review*, Vol. 36, No. 49, page 69. "Cast Iron Sulfur Standards." *Claims evolution sulfur less as sample ages.*
- 1903—A. Klein. *Chem. Ztg.*, Vol. 27, page 729. "Neuerungen im analytischen Arbeiten." *Improved apparatus for evolution method.*
- 1903—N. W. Lord's Book: "Notes on Metallurgical Analysis." 2nd Ed. Ohio State University. 15 pages on sulfur determination.
- 1903—E. Prost's Book: "Manuel d'Analyse Chimique." Beranger, Paris. Pages 309 to 311 on sulfur determination.
- 1903—C. A. Seylor. *Analyst*, Vol. 28, page 97. "Note on the Estimation of Sulfur in Pig-Iron." *Anneals at 750° for 15 min. and uses conc. HCl.*
- 1904—F. L. Crobaugh's Book: "Methods of Chemical Analysis and Foundry Control." On page 59 confirms Dickson and Ireland that evolution sulfur is lower as sample ages.
- 1904—G. T. Dougherty. *Iron Age*, Vol. 73, No. 13, page 3. "The Total Sulfur and Different Forms of Sulfur in Pig and Cast Iron." *Residual sulfur not evolved from some irons until annealed; results on 8 samples.*
- 1904—Ford and Willey. *J. Am. Chem. Soc.*, Vol. 26, page 801. "The Determination of Sulfur in Iron." *Review; criticizes Noyes and Helmar; recommends Bamber's method; precautions.*
- 1904—L. Fricke. *Stahl u. Eisen*, Vol. 24 [2], page 890. "Schwefelbestimmung im Roheisen und Stahl durch Titration mit Jod- und Thio-sulfatlösung." *Follows Kleine and Lunge.*
- 1904—S. S. Knight. *Iron Steel Mag.*, Vol. 7, page 487. "A Rapid Method for the Determination of Total Sulfur in Iron by Evolution." *Anneals in iron dust; no figures.*
- 1904—J. C. Olsen's Book: "Quantitative Chemical Analysis." D. Van Nostrand, N. Y. Pages 351 to 356 on sulfur.
- 1903—C. Friedheim's Book: "Leitfaden für die quantitative chemische Analyse." C. Habel, Berlin. Page 527 gives evolution and colorimetric methods.
- 1905—H. Van F. Furman's Book: "A Manual of Practical Assaying." Wiley, New York, 5th Ed. Chap. II, p. 88. *Compilation of methods.*
- 1905—C. Krug. *Stahl u. Eisen*, Vol. 25, page 887. "Eine Kritik der Schwefelbestimmung im Eisen." *The silver oxide and ether oxidation methods.*
- 1905—C. R. McCabe. *J. Am. Chem. Soc.*, Vol. 27, page 1203. "Note on the Gravimetric Determination of Sulfur in Iron and Steel." *For the oxidation method dissolves sample in reflux flask.*
- 1905—Jacob Petren. *Jern-Kontoreis Annaler*, Vol. 60, page 187. "Om bestämning af svafvel uti järn." *A massive article of 47 pages. Reviews methods critically with fresh material. Many references and tables. Finds concentrated HCl gives correct evolution results.*
- 1905—H. B. Pulsifer. *Chem. News*, Vol. 90, page 230. "A Radically New Method for the Determination of Sulfur in Irons and Steels." *Chloric acid method, weighing as barium sulfate.*
- 1906—McFarlane and Gregory. *Chem. News*, Vol. 93, page 201. "A Modified Evolution Method for the Determination of Sulfur in Pig-Iron." *Anneals with cream of tartar; fine check results.*
- 1906—C. Reinhardt. *Stahl u. Eisen*, Vol. 26, page 799. "Zur Bestimmung des Schwefels im Eisen mit besonderer Berücksichtigung des massanalytischen Verfahrens." 6 pages of discussion, equations, cuts and calculations with no results.
- 1906—J. O. Roos. *Z. anal. Chem.*, Vol. 45, page 782. From Kun. Tek. Høgs. Materialprøfinganstalt, 1896-1906; 34. *Solubility of BaSO₄ in HCl gives error less than 0.002 per cent. at most.*
- 1906—Wilhelm Schulte. *Stahl u. Eisen*, Vol. 26, page 985. "Zur Bestimmung des Schwefels im Eisen." *Very complete article confirms that conc. HCl gives good evolution results.*
- 1907—Arnold and Ibbotson's Book: "Steel Works Analysis." Published by Whittaker & Co., London. Pages 107 to 126 on sulfur determination.
- 1907—E. Dussier. *Stahl u. Eisen*, Vol. 27, page 142. "Zur Bestimmung des Schwefels im Eisen." *Apparatus for evolution method.*
- 1907—von Nostitz and Jankendorf. *Z. anal. Chem.*, Vol. 46, page 157. "Schwefelbestimmungsapparat." *Convenient apparatus for evolution method.*
- 1907—M. Orthey's Book: "Die Eisenhüttenchemie." W. Knall. Gives 7 methods, beginning on page 142.
- 1907—C. F. Sidener's Book: "Quantitative Metallurgical Analysis." H. W. Wilson Co., publishers, Minneapolis. *Sulfur methods page 72, on.*
- 1908—George Auchy. *Chem. Eng.*, Vol. 7, page 87. "Sulfuretted Hydrocarbon Loss in Evolution Methods for Sulfur in Steel and Cast Iron." *Finally admits evolution method may get all sulfur in some cases; 24 results.*
- 1908—R. Bolling. *Eng. News*, Vol. 59, page 505. "The Determination of Sulfur in Pig Iron and Steel by the Hydrogen Jet Method." *Interesting modification of evolution method. Cut of apparatus; 3 comparative results on 8 samples.*
- 1908—Bourrey et Marquet's Book: "Traité d'Analyse Chimique." Published by O. Doin, Paris. Pages 263 to 266 on sulfur methods.
- 1908—J. K. Heess's Book: "Practical Methods for the Iron and Steel Works Chemist." Chem. Pub. Co., Easton, Pa. *Evolution-iodine and nitric acid oxidation methods given.*
- 1908—Isham and Auer. *J. Am. Chem. Soc.*, Vol. 30, page 1236. "Direct Combustion of Steel for Carbon and Sulfur." *Sulfur not wholly available.*
- 1908—H. Kinder. *Stahl u. Eisen*, Vol. 28, page 249. "Schwefelbestimmung im Eisen und Stahl." *Weighty report of commission of German iron association. 5 diagrams, 7 tables with minute discussion and fresh results.*
- 1908—A. Ledebur's Book: "Leitfaden für Eisenhütten Laboratorien." F. Vieweg & Sohn, Braunschweig. 8th edition by W. Heike. *Sulfur on page 112+.*
- 1908—A. Maurice's Book: "Analyse Quantitative des Matières Minérales." Dunod & Pinat, Paris. *Sulfur determination, pages 285 to 301.*
- 1908—B. Neuman's Book: "Post's Chemisch-Technische Analyse." F. Vieweg & Sohn, Braunschweig. Pages 581 to 591 on sulfur methods.
- 1908—M. Orthey. *Z. angew. Chem.*, Vol. 21, pages 1359 and 1393. "Die Bestimmung des Schwefels im Eisen und Stahl." *A monumental exposition of the accuracy of the evolution method. One table has 230 results on 20 samples by 18 different modifications of evolution method.*
- 1908—E. Reymond. *Bull. soc. chim.*, Vol. 22, page 181. "Nouvelle disposition d'appareil pour le dosage du soufre dans les fontes et les aciers." *Apparatus for evolution method.*
- 1908—W. Rosenheim. *J. Iron Steel Inst.*, Vol. 76, Part 1, page 87. "The Metallurgical and Chemical Laboratories in the National Physical Laboratory." *Results by evolution and oxidation methods on 8 samples.*
- 1908—E. Szász. *Stahl u. Eisen*, Vol. 28, page 1466. "Zur Bestimmung des Schwefels in Eisenorten." *Apparatus and details for evolution method.*
- 1909—E. Jaboulay. *Rev. gén. chim.*, Vol. 12, page 190. "Dosage du soufre dans les aciers, fers et fonte." *Neat apparatus with internal condenser.*
- 1909—W. Macfarlane's Book: "Laboratory Notes on Iron and Steel Analysis." Longmans, Green & Co., London.
- 1909—C. G. Mills. *Iron Age*, Vol. 84, page 1318. "Determination of Sulfur in Steel." *Stand for several flasks at once.*
- 1909—A. Schmidt. *Stahl u. Eisen*, Vol. 29, page 1278. "Schwefelbestimmung im Eisen." *One compact evolution apparatus; results on 11 samples.*
- 1909—E. A. Schott. *Stahl u. Eisen*, Vol. 29, page 1444. "Neuer Kolben zur Bestimmung von Schwefel und Kohlenstoff." *Improved evolution flask.*
- 1910—Allen and Johnston. *J. Am. Chem. Soc.*, Vol. 32, page 588. "The Exact Determination of Sulfur in Soluble Sulfates." *An exhaustive investigation in a related field; not of strict application to the minute amounts of sulfur in ferrous materials.*
- 1910—Allen and Johnston. *This Journal*, Vol. 2, page 196. "The Exact Determination of Sulfur in Pyrite and Marcasite." *Separates iron with sodium carbonate.*
- 1910—Anon. *Chem. Ztg.*, Vol. 34, page 231. "Ein vereinfachter Apparat zur Bestimmung des Schwefels im Eisen nach Jenner." *Handy evolution flask.*
- 1910—W. F. Hillebrand. *U. S. Geol. Sur., Bull.* 422, page 193. "The Analysis of Silicates and Carbonate Rocks." *This exposition of the determination of sulfur as BaSO₄, with references, covers many points well.*
- 1910—W. I. Keeler. *Iron Age*, Vol. 86, page 492. "A Modification of the Oxidation Method for Determining Sulfur." *Straight oxidation method with results on 8 samples. No acknowledgments and probably innocent of the extensive literature.*
- 1910—H. Kinder. *Stahl u. Eisen*, Vol. 31, page 1838. "Ueber die Schwefelbestimmung in Roheisen und Stahl." *Evolution method; CdS measured by an iodine-permanganate-thio-sulfate titration.*
- 1910—A. Kleine. *Chem. Ztg.*, Vol. 34, page 636. "Neue Apparate zur Schwefel und Arsen-Bestimmung." *Improved evolution apparatus.*
- 1910—Lunge and Berl's Book: "Chemisch-technische Untersuchungsmethoden." 6th Ed., published by J. Springer, Berlin. Pages 511 to 518 on sulfur determination.
- 1910—Müller and Diethelm. *Z. angew. Chem.*, Vol. 23, page 2114. "Die Bestimmung des Kohlenstoffs und Schwefels in den hochprocentigen Legierungen des Wolframs, Molybdäns und Vanadiums mit Eisen." *Dry combustion best for sulfur.*
- 1910—G. Preuss. *Z. angew. Chem.*, Vol. 22, page 2044. "Apparate zur Schwefelbestimmung in Eisen und Stahl." *Condenser above flask.*
- 1910—G. Preuss. *Z. angew. Chem.*, Vol. 23, page 250. "Apparate

zur Schwefelbestimmung in Eisen und Stahl." *Simplification of previous one as in Z. angew. Chem.*, Vol. 22, page 2044.

1910—G. Preuss. *Z. angew. Chem.*, Vol. 23, page 1980. "Apparate zur Bestimmung des Kohlenstoffs, Arsens und Schwefels in Eisen und Stahl." *Improved evolution apparatus.*

1910—G. Preuss. *Chem. Ztg.*, Vol. 34, page 840. "Neuer Schwefelbestimmungsgesetz." *A very compact outfit.*

1910—A. Rüdtschle's Book: "Die Untersuchungsmethoden des Eisens und Stahls." Published by M. Drechsel, Bern. *Sulfur determination on pages 1 to 48. 175 references partly arranged.*

1910—W. Trautman. *Z. anal. Chem.*, Vol. 49, page 360. "Schwefelbestimmung in Molybdän- und Wolfram-Metall und in deren Eisenlegierungen." *Direct oxidation with oxygen at a red heat.*

1911—Bureau of Standards. *Circular No. 14.* From Department of Commerce, Washington. "Analyzed Irons and Steels—Methods of Analysis." 5th edition in 1916. *Oxidation and evolution methods.*

1911—T. G. Elliott. *Chem. News*, Vol. 104, page 298. "The Volumetric Estimation of Sulfur in Iron and Steel." *Before evolution of H₂S anneals at 800° with K₂Fe(CN)₆. Results on 5 samples.*

1911—T. G. Elliott. *J. Iron Steel Inst.*, Vol. 83, page 412. "The Volumetric Estimation of Sulfur in Iron and Steel." *Optimum temperature for annealing; results on 5 samples.*

1911—Giulitti and Marcantonio. *Rass. min.*, Vol. 35, page 67. From *Chem. Abs.*, Vol. 5, page 3548. *Arnold and Hardy method for rapid sulfur determination.*

1911—D. A. Wennman. *Z. angew. Chem.*, Vol. 24, page 1861. "Neuer Apparat zur Schwefel- und Kohlenstoffbestimmung in Eisen und Stahl." *Improved apparatus for evolution method.*

1911—D. A. Wennman. *Chem. Ztg.*, Vol. 35, page 596. "Neuer Schwefelbestimmungsgesetz." *Improved apparatus for evolution method.*

1911—D. A. Wennman. *Chem. Ztg.*, Vol. 35, page 863. "Apparate zur Schwefelbestimmung in Eisen und Stahl." *Patented evolution apparatus.*

1912—Bauer and Deiss's Book: "Probenahme und Analyse von Eisen und Stahl." J. Springer, Berlin. *Gives three of best methods.*

1912—A. A. Blair's Book: "The Chemical Analysis of Iron." 7th Ed., Pub. by Lippincott's, Philadelphia. *The leading American treatise on the subject.*

1912—L. Brandt. *Stahl u. Eisen*, Vol. 31, page 1935. "Zur Schwefelbestimmung in Eisen und Stahl." *Discussion and cut of absorption bulbs for evolution method.*

1912—The Chemists' Committee of the U. S. Steel Corporation. *8th Internat. Congr. Appl. Chem.*, Vol. 1, page 91. "The Methods of the United States Steel Corporation for the Commercial Sampling and Analysis of Pig Irons." *Customary evolution and oxidation processes given.*

1912—C. Krug's Book: "Die Praxis des Eisenhüttenchemikers." J. Springer, Berlin. *Page 113+ gives methods for sulfur.*

1912—Spang. *Chem. Ztg.*, Vol. 36, page 392. "Vereinfachter Apparat zur Bestimmung des Schwefels in Eisen und Stahl." *Improved evolution apparatus.*

1912—Treadwell and Hall's Book: "Analytical Chemistry, Vol. II, Quantitative Analysis." Wiley and Sons, New York. *Pages 350 to 366 on sulfur determination. This is 3rd edition; 4th edition in 1916.*

1912—Vita and Massenez. *Stahl u. Eisen*, Vol. 32, page 2089. "Eine neue Schwefelbestimmung in Roheisen und Stahl." *Oxidation of H₂S from evolution method with permanganate titration.*

1913—H. Beckurts's Book: "Die Methoden der Massanalyse." F. Vieweg & Sohn, Braunschweig. *Methods for sulfur determination begin on page 298.*

1913—Wm. W. Clark. *Met. Chem. Eng.*, Vol. 11, page 256. "The Determination of Sulfur in Ferro-Vanadium." *Wet or dry oxidation method must be used.*

1913—Fischer. *Chem. Ztg.*, Vol. 37, page 1223. "Eine Abänderung des Schultschen Schwefelbestimmungsgesetzes für Rohisen und Stahl." *Air does not oxidize H₂S; results on 12 samples.*

1913—F. H. Franklin. *THIS JOURNAL*, Vol. 5, page 839. "A Fusion Method for the Determination of Sulfur in Iron and Steel." *Dissolves in Cu-K-Ba-chloride solutions with fusion of residue and final weighing as BaSO₄. Few results given and one step questionable.*

1913—Lord and Demorest's Book: "Metallurgical Analysis." McGraw-Hill Book Co., New York. 3rd edition, Chapter VII, "The Determination of Sulfur." *Excellent directions, modifications, criticisms and references. 4th edition, 1916.*

1913—G. Preuss. *Chem. Ztg.*, Vol. 37, page 82. "Apparat zur Schwefelbestimmung in Stahl und Eisen." *Improved evolution apparatus.*

1913—Vita u. Massenez's Book: "Chemische Untersuchungsmethoden für Eisenhütten und deren Nebenbetriebe." J. Springer, Berlin. *Sulfur methods begin on page 74.*

1914—Grant. *Chem. Analyst*, Vol. 9, page 9. *Evolution method with absorption in cupric nitrate and colorimetric estimation.*

1914—C. M. Johnson's Book: "Rapid Methods for the Chemical Analysis of the Special Steels, Steel-Making Alloys and Graphite." *Cites where evolution method fails and how overcome; little new but several popular fallacies included.*

1914—G. Misson. *J. Iron Steel Inst.*, Vol. 89, Part 1, page 510. "The Colorimetric Estimation of Sulfur in Pig Iron and Steel." *As₂O₃ in HCl gives a yellow color on paper discs in special apparatus. Several results.*

1914—W. A. Turner. *Am. J. Sci.*, Vol. 38, page 41. "An Improvement of the Barium Sulfate Determination of Sulfur in Soluble Sulfates when Sodium Salts are Present." *Precipitates the alkali with HCl and washes with same; evaporates and ppt. BaSO₄.*

1915—Bauer and Deiss, translated by Hall and Williams, Book: "The Sampling and Chemical Analysis of Iron and Steel." McGraw-Hill Book Co., New York. *Excellent on segregation, sampling and methods; thus a very important contribution to the subject.*

1915—B. Osann's Book: "Leitfaden für Giessereilaboratorien." J. Springer, Berlin. *Gives Schulte's method.*

1915—F. C. Phillips's Book: "Methods for the Analysis of Ores, Pig Iron and Steel." 2nd edition, reprint. Chemical Publishing Co., Easton, Pa. *Individual methods of laboratories in Pittsburgh district.*

1915—C. H. White's Book: "Methods in Metallurgical Analysis." D. Van Nostrand Co., New York. *Bamber's and evolution methods given; scant mention of fine points of segregation, sampling and anal.*

1916—H. Zschiegnier. *THIS JOURNAL*, Vol. 8, page 324. "An Accurate End-Point in the Volumetric Determination of Sulfur in Steel." *Uses a black spot in a white porcelain beaker; usual iodine titration.*

A MODIFICATION OF PRICE'S METHOD FOR THE SEPARATION OF THE SEVEN PERMITTED COAL-TAR DYES TO INCLUDE TARTRAZINE¹

By CLARENCE ESTES

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Food Inspection Decisions 76, 117 and 129 of the United States Department of Agriculture have been amended by *Food Inspection Decision* 164, so that hereafter, the following 8 coal-tar dyes may be used to color food products, subject to the provision of *Food Inspection Decisions* 76, 117 and 129: 107-Amaranth, 56-Ponceau 3R, 517-Erythrosin, 85-Orange I, 4-Naphthol Yellow S, 435-Light Green S F Yellowish, 692-Indigo Disulfonic Acid, and 94-Tartrazine.

A method for the separation of the first seven coal-tar dyes, when occurring in mixtures, has been worked out by Price, which depends upon the solubility or insolubility of the dyes in various solvents, but so far as the writer is aware, there has not been published a method for the separation of the eight permitted coal-tar dyes. I wish, therefore, to give a modification of Price's scheme to include the new permitted coal-tar dye Tartrazine.

THE REAGENTS are the same as those given by Price with the addition of glacial acetic acid and concentrated hydrochloric acid.

PROCEDURE—Assuming that the dyes occur together in a food product and it is desired to separate and identify them, it is first necessary to separate the dyes from the food products by slightly acidifying an aqueous solution of the material with hydrochloric acid; then add a piece of white woolen cloth, which has been freed from grease, and boil until most of the color has been removed. Remove the dyed cloth and rinse thoroughly in boiling water to remove any foreign material which may be adhering to the fiber. The dyes are stripped from the cloth by immersing in a very dilute solution of ammonia and boiling. When stripping of the dye from the cloth is complete, acidify and repeat the dyeing process with a new piece of cloth if fruit colors are present; remove the cloth after the second stripping and evaporate to dryness on a water bath. This leaves the dyes in a pure dry condition ready for the separation.

Rub a small quantity of the dyes in an evaporating dish with about 25 cc. of supersaturated solution of ammonium sulfate, filter, and wash the residue with small portions of the supersaturated solution of ammonium sulfate until the washings are no longer colored red. The filtrate and washings will contain *Amaranth*, *Tartrazine* and a small quantity of *Naphthol Yellow S*. The *Naphthol Yellow S* is separated from *Amaranth* and *Tartrazine* by extracting several times with ethyl acetate until it is no longer colored yellow. The ethyl acetate extract containing the *Naphthol Yellow S* is discarded, as it will be separated in a pure state later. *Amaranth* and *Tartrazine* are separated from the ammonium sulfate by extracting with acetone. The acetone solution is diluted with water and evaporated on a steam bath until the acetone has been expelled.

¹ U. S. Department of Agriculture, Bureau of Animal Industry, *Bull.* 180.