the suspicions regarding the men's guilt would be confirmed.

The results, however, entirely exonerated the men from all blame and showed the cause to be due to the poor burning quality of the ore itself. At that time I did not have the electric furnace, but made the determinations in one and the same dish placed on a tripod and heated with a small Méker burner, shielded from draughts by a sheet iron hood. The results were as given in Table IV.

EUSTIS LUMP ORE ACTUAL ANALYSIS			CARRIDAD ORE ACTUAL ANALYSIS		
A—Sulfur in ore.....	45.8%		A—Sulfur in ore.....	43.7%	
B—Sulfur in cinders.....	3.0%		B—Sulfur in cinders.....	9.7%	
CALCULATION FROM A			CALCULATION FROM A		
$a = \frac{45.8}{100} \times 2 = 0.9160$			$a = \frac{43.7}{100} \times 2 = 0.8740$		
t	$a - x$	K_{10}	t	$a - x$	K_{10}
15	0.3705	0.02620	15	0.5027	0.01601
30	0.1893	0.02282	30	0.3243	0.01435
45	0.0446	0.02916	45	0.1945	0.01450
Average K_{10}	0.02606		Average K_{10}	0.01495	
$\therefore K_e = 2.30259 K_{10} = 0.06001$			$\therefore K_e = 2.30259 K_{10} = 0.03442$		
$(100 - x + \frac{48}{128.24} x) : (45.8 - x)$			$\frac{2.30259}{51} \log \frac{43.7}{a-x} = 0.03442$		
$= 100 : 3$			$a - x = 7.55$ g. Sulfur in cinders		
$a - x = 2.18$ g. Sulfur in cinders			$x = 36.15$ Available Sulfur burnt off		
$x = 43.62$ g. Sulfur burnt off			$a = 43.70$		
$a = 45.80$			$100 - 36.15 + \frac{48}{128.24} \times 36.15$		
$\frac{2.30259}{t} \log \frac{45.8}{2.18} = 0.06001$			$= 76.91$ per cent cinder		
$t = 51$ minutes			$\frac{7.55}{76.91} \times 100$		
			$= 9.80$ per cent sulfur in cinders		

Again in November that same year some of this Carridad ore was burned as fines with such unusual low sulfur test in the cinders, compared with the lump ore, that now the suspicion arose as to the accuracy of the cinder samples or the cinder test. Again, the determination of the rate of change of the fines ore exonerated the parties concerned, and placed the explanation on the better burning qualities of the fines ore. As it was not any surety that the flame could be adjusted to the exact conditions prevailing when the test of the lump ores was made the preceding August, I chose for comparison a sample of Eustis fines ore burned the same month as the Carridad fines. The results are given in Table V.

EUSTIS FINES ORE ACTUAL ANALYSIS			CARRIDAD FINES ACTUAL ANALYSIS		
A—Sulfur in ore.....	46.1%		A—Sulfur in ore.....	42.2%	
B—Sulfur in cinders.....	2.6%		B—Sulfur in cinders.....	2.1%	
CALCULATION			CALCULATION		
$a = \frac{46.1}{100} \times 2 = 0.9220$			$a = \frac{42.2}{100} \times 2 = 0.8440$		
t	$a - x$	K_{10}	t	$a - x$	K_{10}
15	0.3962	0.0247	15	0.3628	0.0245
30	0.2120	0.0214	30	0.1941	0.0213
45	0.0675	0.0253	45	0.0621	0.0252
Average K_{10}	0.0238		Average K_{10}	0.0236	
$\therefore K_e = 2.30259 K_{10} = 0.0548$			$\therefore K_e = 2.30259 K_{10} = 0.0543$		
$(100 - x + \frac{48}{128.24} x) : (46.1 - x)$			$\frac{2.30259}{58} \log \frac{42.2}{a-x} = 0.0543$		
$= 100 : 2.6$			$a - x = 1.80$ g. Sulfur in cinders		
$x = 44.22$ g. Sulfur burnt off			$x = 40.40$ g. Available Sulfur burnt off		
$a - x = 1.88$ Available Sulfur left in cinders			$a = 42.20$		
$a = 46.10$			$100 - 40.4 + \frac{48}{128.24} \times 40.4$		
$\frac{2.30259}{t} \log \frac{46.1}{1.88} = 0.0548$			$= 74.72$ g. cinders		
$t = 58$ minutes			$\frac{1.80}{74.72} \times 100$		
			$= 2.40$ per cent sulfur in cinders		

CONCLUSION

It is well known that as regards available sulfur in pyrites no method has hitherto been presented that does at all agree with practice.

To account for the low yield of available sulfur it is the custom in some places at least, to determine such heavy metals as lead, copper and zinc and deduct from the total sulfur that equivalent to sulfates of these metals, but even so, there is usually no agreement with practical yields and as the sulfates of these heavy metals are all decomposable at a bright red heat, the temperature of the burners, it is evident that such a practice is faulty, even if it occasionally should seem to agree with practical results.

The only reliable method of arriving at the available sulfur content of a pyrites is, as has been shown, the determination of the rate of change of the ore, compared with some other ore that works normally and the available sulfur of which is known.

Furthermore, this determination serves as a check upon results already obtained and so helps to place the true explanation upon them instead of subjecting them to mere suspicions, which, though seemingly reasonable, may still be untrue.

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A CONVENIENT APPARATUS FOR ELECTROMETRIC TITRATION DEPENDING ON THE CHANGE OF OXIDATION POTENTIAL, AND ITS APPLICATION TO THE DETERMINATION OF SMALL QUANTITIES OF CHROMIUM IN STEEL

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THE APPARATUS

The apparatus for electrometric titration described by Hildebrand¹ and Forbes² and the modified form described by Kelley and Conant³ consisted of a number of separate parts, many of which were not well adapted to purposes to which they were put. In the present apparatus, which was made for us by Leeds and Northrup, the parts have been selected to give the greatest efficiency for such work and are combined as a unit in a single rugged instrument. The present instrument can be moved about the laboratory readily, requiring for its operation only the connection of a plug with an electric light socket. It is complete in that it carries a potentiometer system, a motor for the operation of the stirrer and the two burettes for the oxidizing and reducing solutions.

ILLUSTRATION

As will be seen in the illustration, the apparatus consists essentially of a wooden box with a metal upright carrying the motor, burettes and electrodes. In the box are two dry cells, an adjustable resistance and a Leeds and Northrup reflecting galvanometer of the form known as Type 2400. This galvanometer is sufficiently sensitive for the purpose and has the further advantage of a very short period. On the

¹ J. Am. Chem. Soc., **35** (1913), 869.

² Ibid., **35** (1913), 1527.

³ Ibid., **38** (1916), 341.

upper surface of the box is a ground glass plate on which the light from the galvanometer is thrown. This puts it in a position where it may be conveniently observed by the operator during titration. A knob on top of the box permits of adjusting the zero point of the galvanometer and one on the side controls the resistance. A plug and resistance coil, also on the side, make it possible to vary the resistance and so increase the range of potentials over which the adjustable resistance may be made to operate. The standard carries the burettes,

the electrodes, and the motor for driving the stirrer. In addition, provision has been made for a reservoir of the electrolyte which is used in the calomel cell (a concentrated solution of potassium or sodium nitrate and calomel) to make conveniently possible without change in its potential the displacement of the impure electrolyte which may have accumulated in the tip of the calomel electrode. This is accomplished by opening the stopcock at the top of the electrode enough

to let one or two drops pass. A hard rubber pan, carried on an adjustable support, serves to center the beaker in which the titration is made, and because of stops prevents carrying the beaker high enough to strike the electrodes or stirrer. Two switches are mounted on the box. One controls the motor and galvanometer light and the other throws in the potentiometer circuit. All connections, except to dry cells, are soldered and the insulation is designed to make as little as possible trouble from "leaks."

To operate the instrument, a beaker containing the solution to be analyzed is placed on the rubber pan, and the support raised and locked in position. The switch controlling the galvanometer light and motor is then closed. The other switch closes the potentiometer circuit and a slight turn of the knob controlling the resistance is sufficient to bring the beam of light from the galvanometer onto the scale. In titrating a series of solutions at one time this latter adjustment need be made only once. During the operation, which is quick, certain and convenient, the analyst watches the beam of light until a permanent change of potential is noted. The apparatus has been in satisfactory daily use in this laboratory for several months for the determination of chromium and vanadium in steel and ferro alloys.

THE DETERMINATION OF SMALL AMOUNTS OF CHROMIUM IN STEEL

Many methods for the determination of chromium in steel make possible the determination of this element to within 0.01 or 0.02 per cent of the weight of the sample. Other more rapid methods show variations amounting to 0.10 per cent. In this paper we give figures showing that determinations may be made which agree within 0.001 per cent and which are probably accurate to nearly this degree. This has been made possible by the development of the instrument described above. In a paper by one of us¹ chromium determinations on a given sample are shown as varying by several hundredths of a per cent. With this instrument and solutions of the same strength, these differences have been reduced to 0.01 per cent. By using more dilute solutions in the analysis of samples containing small amounts of chromium, the determinations were made with a corresponding degree of accuracy.

A standard chromate solution was prepared of such strength that one liter of solution contained 1 gram of chromium. Twice crystallizing potassium dichromate of C. P. grade, powdering and drying it at 150° for several hours gives a product from which solutions may be made accurate to 1 part in 500. If it is desired to standardize such a solution with permanganate to a color end-point, the most convenient procedure is to standardize the permanganate by titration against sodium oxalate. This is next compared with ferrous sulfate and the chromate is finally titrated by adding an excess of ferrous sulfate and titrating back with permanganate. Care must be taken to obtain corrections on blank titrations for all end-points. With-

¹ THIS JOURNAL, 8 (1916), 719.

out such corrections, the error may amount to 7 to 10 parts in 1000, the figure for chromium appearing too low by this amount. Even when sodium phosphate is used the correction is necessary. It has been the custom in this laboratory to prepare a blank by reducing the chromate solution with SO_2 in hot solution, after which it is boiled gently for 15 min. while a stream of CO_2 is passed in. The solution is then cooled, diluted to the proper volume and permanganate added gradually to the first permanent change in color. During the reduction material reducible by SO_2 other than chromates must be carefully excluded and the presence of halogens is to be avoided also because of the action on the permanganate. Another method of finding this blank consists in adding a quantity of standard ferrous sulfate solution to the solution of chromic salt, which upon titration will be found to have required an amount of permanganate too large by the amount of the correction. The end-point obtained has a color which is described as blue by some and as gray by others. It appears much earlier than the first pink color and it is a more definite point. This method of obtaining the blank is somewhat questionable because the color of the solution of chromic salts is noticeably different from that which results from the reduction of chromates by ferrous sulfate.

If all titrations, except the titration of sodium oxalate with permanganate, are made on the electrometric apparatus, better results are obtained. On this apparatus one may titrate, (1) permanganate and ferrous sulfate, (2) chromate and ferrous sulfate, and (3) chromate, using an excess of ferrous sulfate with respect to the chromate, completing the titration with permanganate and ferrous sulfate. In working with different combinations of oxidizing and reducing reagents on this apparatus, we have noted certain characteristic differences at the end-point. Allowance must be made for this if full advantage is to be taken of the accuracy of which the instrument is capable. In titrating a chromate solution the addition of ferrous sulfate almost invariably produces what Forbes describes as an anomalous rise. In titrating a permanganate solution, this phenomenon does not appear with quite the same regularity and is always less marked. In titrating chromate, the change in potential is always abrupt when the end-point is reached, but with permanganate the addition of as many as 0.2 to 0.4 cc. of ferrous sulfate after the disappearance of the pink color often causes only a gradual change. If now permanganate be added drop by drop the return of the original potential is delayed until one or two drops cause a marked change. One or two additional drops of permanganate are now sufficient to produce a pink color. From this point the titration of the permanganate with ferrous sulfate closely resembles the titration of chromates, in that no change occurs until the end-point is reached when the change is abrupt. It has occurred to us that in adding ferrous sulfate gradually to an excess of permanganate, a suspension of manganese dioxide is built up which requires an appreciable excess of ferrous sulfate for its reduction. On titrating back with permanganate, either the condition is overcome,

or it is so much less marked as to have no appreciable effect upon the behavior of the electrodes. It is our custom to add ferrous sulfate in excess until there is a marked change of potential. Permanganate is then added gradually until the original potential is reached which existed immediately before the fall in potential began or until the further addition of two or three drops causes no further change. The drop-wise addition of ferrous sulfate then gives a sharp and definite end-point.

In connection with the analyses given in this paper 100 cc. of the solution of chromate containing 1 g. Cr in a liter was diluted to 1000 cc. A solution of ferrous sulfate of equivalent strength was similarly diluted. When these solutions were compared their relation was found to be unchanged. These solutions were of such strength that 0.1 cc. corresponded to 0.001 per cent of Cr in a 1 g. sample of steel or to 0.0005 per cent in a sample weighing 2 g. The samples were prepared for titration exactly as described elsewhere.¹

In the table below, we give analyses for chromium on samples of steel issued by the Bureau of Standards. The column marked "Certif. Value" contains the percentage of chromium given on the certificate; it is not known what accuracy is claimed for these figures, but it is probably not greater than 0.003 or 0.004 per cent. In the case of Sample 33, one analyst reports 0.11 and another 0.12.

SAMPLE PER CENT CHROMIUM				SAMPLE PER CENT CHROMIUM			
B. of S. No.	Grams Taken	Certif. Value	Found Electr. Titr.	B. of S. No.	Grams Taken	Certif. Value	Found Electr. Titr.
10b.....	2	0.005	0.007(2)	33..	2	0.11 and 0.12	0.113(5)
	3		0.007(2)				
	2		0.007(0)		2		0.113(5)
	3		0.007(7)		3		0.113(3)
16a.....	2	0.008	0.009(5)		3		0.113(7)
	2		0.009(5)				
19a.....	2	0.08	0.076(5)	34..	2	0.01	0.011(5)
	2		0.076(7)		2		0.011(5)
	3		0.076(5)		3		0.011(3)
	3		0.076(3)		3		0.011(5)

We believe this to be the most sensitive and accurate method known for the determination of small amounts of chromium in complex solutions. Of substances ordinarily present in steel, only vanadium interferes.

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THE PHOTOMICROGRAPHY OF PAPER STRUCTURE

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In the study of the ultimate structure of paper, much valuable information can be obtained by photomicrographs of cross-sections of the paper stocks.

Some published accounts have appeared from time to time illustrating the matting together of fibers in paper stocks, but little has been done in the direction of a more intimate study of the subject, and the possibility of data to be obtained from photomicrographs of cross-sections of paper has scarcely been touched upon, one reason for the lack of work in this last direction probably being the difficulty of making cross-sections of paper.

¹ Loc. cit.