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A RAPID METHOD OF CORRECTING FUEL VALUE DETERMINATIONS USING THE OXYGEN BOMB CALORIMETER

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In making fuel value determinations with the oxygen bomb calorimeter it is necessary to correct the observed fuel value by subtracting the heat of combustion of the fuse wire and the heats of formation of the acids present after combustion. Nitric and sulfuric acids are formed by the following reactions which are not possible in furnace combustion.

$$\tfrac{1}{2}\,N_2 + \tfrac{5}{4}\,O_2 + \tfrac{1}{2}\,H_2O = HNO_3 \qquad \triangle H = -1863 \text{ Btu}$$

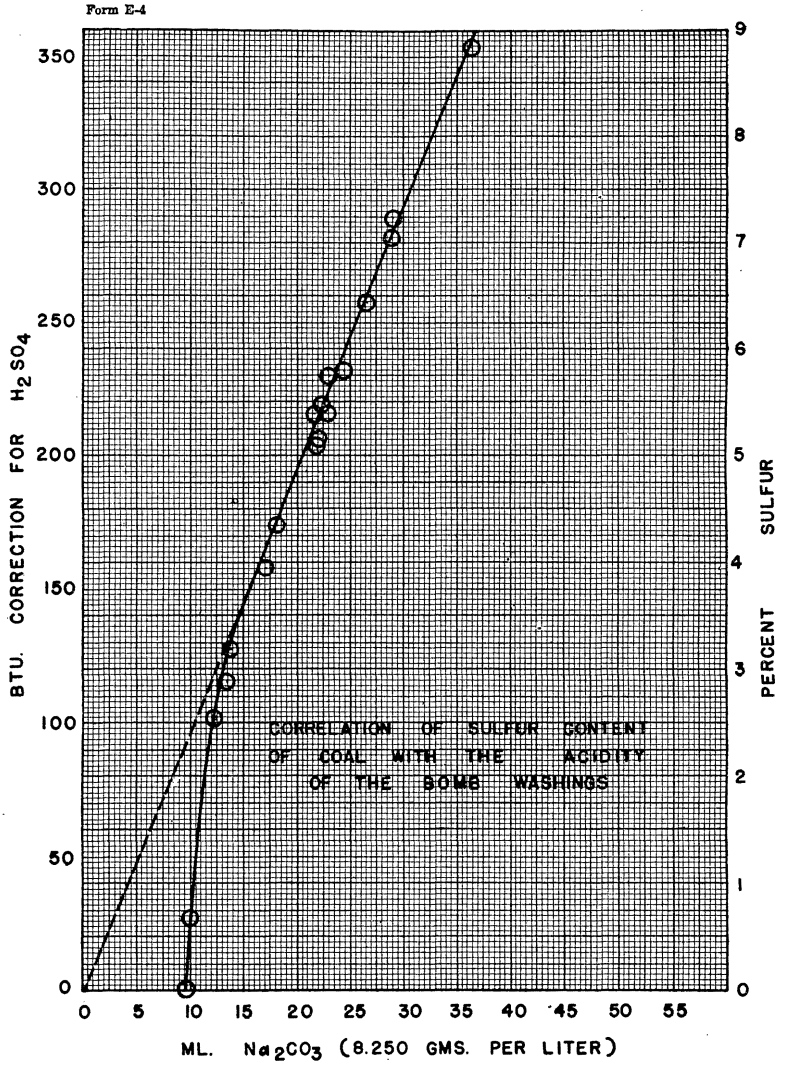
$$SO_2 + \tfrac{1}{2}\,O_2 + H_2O = H_2SO_4 \qquad \triangle H = -4007 \text{ Btu}$$

In making the acid corrections, it is customary to titrate all of the acid washed from the bomb, correct the fuel value as though all the acid were nitric, determine sulfur gravimetrically or with a turbidimeter, and make an additional correction based upon the difference between the sulfur content and the allowance already made as nitric acid (1, 3).

Since the determination of sulfur content is troublesome when speed is necessary, the method outlined by Kaufman (2) was investigated. He found it possible to derive a straight line relationship between the sulfur content of fuel oils and the total acidity of the bomb washings which was accurate to within 10 Btu's.

We have found it possible to treat similarly bituminous coal samples from Iowa and Illinois as can be seen with reference to the figure. The standard sodium carbonate solution used was made up to 8.250 grams per liter so that 1 ml. was equivalent to 10 Btu's per pound caused by the oxidation of sulfur dioxide to sulfuric acid and to 3.7 Btu's per pound caused by the oxidation of nitrogen to nitric acid.

In the region above 3½ percent sulfur content, the data lie on a straight line having a slope of 0.25 percent per ml. and by extrapolation a zero intercept. This indicates that there was substantially no nitric acid present in the solution throughout this region. This was verified by qualitative tests for the nitrate radical. Oxides of nitrogen may have been present in the escaping



gas, for on occasions it was possible to smell them, but little or none of it dissolved and consequently did not influence the titration.

The data plotted in the figure lie within 10 Btu of the curve so it may be used to obtain fuel value corrections of that accuracy from the titration of the bomb washings directly. The A.S.T.M. tolerance on fuel value determinations (1) is 0.3 percent, that is, 30 Btu's on a fuel value of 10,000 Btu per pound. The A.S.T.M. tolerance on sulfur determinations, however, is 0.10 percent for

coal having more than 2 percent sulfur content. The data indicate that the figure is accurate to only 0.25 percent on coals having more than 3½ percent sulfur content, so sulfur determinations must be made by one of the other methods.

Below 3½ percent sulfur content, nitric acid was present in the bomb washings to a predominating extent. Much of it arises from oxidation of the elementary nitrogen from the air which remains in the bomb upon closing. The extent of this reaction depends upon the pressure in the bomb so that consistent results can be expected only at a standard pressure. All of the tests in this laboratory were run at 25 atmospheres oxygen pressure. The point plotted as zero percent sulfur was calculated by adding the equivalent of one percent nitrogen to the blank obtained from benzoic acid combustions. Since the nitrogen content of most coals lies between 0.8 percent and 1.2 percent the curve indicates that the bulk of the combined nitrogen is oxidized and dissolved when the sulfur content is low.

In the region below 3½ percent sulfur content a correction must be made for both the sulfuric and the nitric acid present. This may be done with the aid of the figure, but the accuracy in this region is uncertain, and should perhaps not be relied upon.

This investigation has been limited primarily to Iowa and Illinois coal screenings, some lump samples and a few eastern coals. Other varieties may need to be correlated separately.

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