SCIENCE:

PUBLISHED BY N. D. C. HODGES, 874 BROADWAY, NEW YORK.

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IRON AND ALUMINIUM IN BONE BLACK: THEIR QUANTITATIVE DETERMINATION.

BY DR. F. G. WIECHMANN, COLUMBIA COLLEGE, NEW YORK.

THE determination of iron and aluminium in bone black has thus far been commonly effected by the so-called ammonia-acetate method, which, until quite recently, has also been the favorite method employed for the determination of the constituents mentioned in mineral phosphates.

As this method, however, is open to serious objections, it was decided to test its accuracy, and to compare the results obtained with those yielded, respectively, by the method of E. Glaser,[1] and by the combination of Glaser's method with that of A. Stutzer,[2] first suggested by R. Jones[3] for the analysis of fertilizers.

For valuable analytical work performed in this connection, the writer's thanks are due his assistant, Mr. E. C. Brainerd.

The schemes of analysis used in this investigation are minutely given in the following directions: —

Method I. Acetate of ammonia process.

(This method is based on the solubility of calcium phosphate in acetic acid, and on the insolubility of the phosphates of iron and aluminium in this medium.)

1. Powder sample. 2. Dry thoroughly. 3. Weigh out 3.0 grammes. 4. Dissolve in distilled water + 25 cubic centimetres HCl (conc.), boiling gently for one hour. 5. Filter. 6. Wash residue on filter, until the wash-water no longer reacts for Cl with $Ag NO_3$. 7. Add excess of $Ba Cl_2$, boil till $Ba SO_4$ is granular. 8. Filter. 9. Wash the $Ba SO_4$ on the filter till no more reaction for Cl with $Ag NO_3$. 10. To filtrate and wash-waters combined add NH_4OH, until the precipitate formed begins to appear permanent. 11. Then add acetic acid to pronounced acid reaction, and boil. 12. Filter. 13. Wash the precipitate well. 14. Dry, ignite, weigh. 15. Regard the precipitate as $Fe PO_4 + Al PO_4$, calculate to $Fe_2 O_3 + Al_2 O_3$, and so report.

Method II. Glaser's method.

(In this process the calcium is removed from an alcoholic solution by means of sulphuric acid before the precipitation of the iron and aluminium is effected.)

1. Powder sample. 2. Dry thoroughly. 3. Weigh out 5 0 grammes. 4. Dissolve in distilled H_2O + 30 cubic centimetres $H Cl$ (conc.) + 10 cubic centimetres $H NO_3$ (conc.). 5. Make the solution up to 500 cubic centimetres with distilled water. 6. Filter. 7. Of the filtrate take 100 cubic centimetres (equal to 1.00 gramme), place in a 250 cubic centimetre flask, add 25 cubic centimetres $H_2 SO_4$ (conc.). Shake frequently, and allow to stand for five minutes. 8. Add absolute ethyl alcohol, cool, fill up to the mark with alcohol, and shake well. 9. As volume contraction will take place, fill up to the mark repeatedly with alcohol, and shake each time. Continue this filling up to the mark until no more contraction takes place. 10. Allow the solution to stand for 12 hours. 11. Filter. 12. Of the filtrate take 100 cubic centimetres (= 0.4 gramme), place in a large platinum dish on a water-bath, and heat until all the alcohol is removed. 13. Wash the remaining solution into a beaker with 50 cubic centimetres of distilled water. 14. Heat to boiling, and then remove the flame. 15. Add NH_4OH very carefully to alkaline reaction. 16. Boil until the ammonia is completely expelled. 17. Filter. 18. Wash the precipitate thoroughly with boiling, distilled water. 19. Dry, incinerate, weigh. 20. Regard the precipitate as $Fe PO_4 + Al PO_4$, calculate to $Fe_2 O_3 + Al_2 O_3$, and so report.

Method III. Combination of the methods of Glaser and Stutzer.

(Stutzer's method consists essentially in precipitating the iron and aluminium, principally as phosphates, in a solution of ammonium acetate; treating this precipitate with a solution of ammonium molybdate, to remove the phosphoric acid as phospho-ammonium molybdate; filtering out this precipitate, and in the resulting filtrate precipitating the iron and aluminium as hydrates, by ammonium hydrate; drying and igniting this precipitate, weighing it as $Fe_2 O_3 + Al_2 O_3$, and reporting it as such.)

The following scheme, it is believed, offers all the advantages of both the Glaser and the Stutzer methods.

Proceed exactly as in Method II. up to and inclusive of section No. 18.

Then continue as follows: —

1. Place filter and contents in a beaker which contains 150 cubic centimetres molybdic solution,[4] at a temperature of about 40° C. 2. Keep the mixture at a temperature of about 65° C. for from 12 to 15 hours. 3. Filter out the precipitate. 4. Wash the precipitate thoroughly with $NH_4 NO_3$ solution (1 : 10). 5. To filtrate add $NH_4 OH$ till it is well alkaline. 6. Heat for 2 or 3 hours over a gentle flame, replacing any loss by evaporation by the addition of water and ammonic hydrate. 7. Filter out the precipitate. 8. Dissolve this precipitate from the filter with $H Cl$. 9. Precipitate with NH_4OH, and boil out all free ammonia. 10. Filter. 11. Wash precipitate, dry, incinerate, and weigh. 12. Regard the precipitate as $Fe_2 O_3 + Al_2 O_3$, and so report.

The mixture on which these three methods were tested consisted of: —

Tri-calcic phosphate...	20.00 grammes
Aluminium sulphate..............	0.10 "
Ferrous sulphate...................	0.10 "

These amounts of the sulphates of iron and aluminium corresponded to 0.67 per cent of $Fe_2 O_3 + Al_2 O_3$, as was ascertained by analysis.

The mixture was dissolved in $H_2 O + H Cl$, and made up to 500 cubic centimetres. 24.75 cubic centimetres of this solution contain 1.00 gramme of the dry substance.

In Method I., used 3.00 grammes; in Method II., 1.00 gramme; in Method III., used 1.00 gramme of the "dry substance" for analysis.

Results of Analysis.

		Method.		
		I.	II.	III.
		Per cent.	Per cent.	Per cent.
$Fe_2 O_3 + Al_2 O_3$	Present	0.67	0.67	0.67
	Found	0.56	0.60	0.63

Method I. has evidently yielded the least satisfactory result.

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[1] Zeitschrift für Angewandte Chemie, 1889, p. 636.

[2] Zeitschrift für Angewandte Chemie, 1890, p. 43.

[3] Chemiker Zeitung, 1890, p. 269.

[4] Dissolve 100 grammes molybdic acid in 40 grammes, or 417 cubic centimetres of ammonium hydrate (sp. gr. 0.96), and pour the solution thus obtained into 1500 grammes, or 1250 cubic centimetres, of nitric acid (sp. gr. 1.20). Keep in a warm place for several days, decant the solution from any sediment, and preserve in glass-stoppered vessel.

Examining into its merits, it is readily seen that this method, as previously stated, is open to several serious objections: phosphate of aluminium is quite soluble in an excess of acetic acid; the precipitate of the phosphates of iron and aluminium is very apt to carry with it some of the calcium salt; the precipitate of the iron and aluminium obtained is not necessarily pure normal ortho-phosphate; and, finally, there is a great risk of introducing an error in calculating the combined phosphates of iron and aluminium over to the sesqui oxides.

The molecular masses of the compounds concerned are:—

$$\begin{aligned} Fe\ PO_4 &= 151 \\ Al\ PO_4 &= 122 \\ Fe_2\ O_3 &= 160 \\ Al_2\ O_3 &= 102 \end{aligned}$$

If the constituents, the iron and the aluminium phosphates, occur in the precipitate in the proportion of their respective molecular masses, i.e., 151 : 122, no error will be committed in assigning to this precipitate of the mixed phosphates the formulæ, ($Fe\ PO_4 + Al\ PO_4$), and calculating to $Fe_2\ O_3$, as is shown by the following example. Assume the composition of the precipitate to be:—

$$\begin{aligned} Fe\ PO_4 &= 0.151 \\ Al\ PO_4 &= \underline{0.122} \\ Fe\ PO_4 + Al\ PO_4 &= 0.273 \end{aligned}$$

Calculating the combined phosphates over to the combined oxides:—

$$\begin{array}{ccccc} 2\ (Fe\ PO_4 + Al\ PO_4) & : & (Fe_2\ O_3 + Al_2\ O_3) & :: & .273 : x \\ 546 & : & 262 & :: & .273 : x \\ & & x = 0.131 & & \\ \multicolumn{5}{c}{\text{i.e., } (Fe_2\ O_3 + Al_2\ O_3) = 0.131} \end{array}$$

Calculating the Fe PO_4 and the Al PO_4 separately over to their respective oxide, and then adding them:—

$$\begin{array}{l} 2\ Fe\ PO_4 : Fe_2\ O_3 :: 0.151 : x \\ \quad 302 \ :\ 160 \ :: 0.151 : x \\ \quad x = 0.080 \quad Fe_2\ O_3 \\ 2\ Al\ PO_4 : Al_2\ O_3 :: 0.122 : x \\ \quad 244 \ :\ 102 \ :: 0.122 : x \\ \quad x = 0.051 \quad Al_2\ O_3 \end{array}$$

$$\begin{array}{l} 0.0800\ Fe_2\ O_3 \\ \underline{0.0510\ Al_2\ O_3} \\ 0.1310\ Fe_2\ O_3 + Al_2\ O_3, \end{array}$$

which is identical with the value previously obtained. If, however, the iron phosphate and the aluminium phosphate are present in a proportion different from the one assumed in the above example, the result obtained by calculating their combined weight to combined oxides is wrong. It will be too high or too low, accordingly as the iron, aluminium, or the phosphate predominates.

Example.—Assume that the combined phosphates weighed exactly the same as before = 0.273 gramme; but assume the composition of the precipitate to be:—

$$\begin{aligned} Fe\ PO_4 &= 0.219 \\ Al\ PO_4 &= \underline{0.054} \\ &\ 0.273 \end{aligned}$$

Calculating the combined phosphates over to the combined oxides, of course the same result as previously found will be obtained, namely, that

$$\begin{array}{ccc} 0.273 & = & 0.131 \\ (Fe\ PO_4 + Al\ PO_4) & & (Fe_2\ O_3 + Al_2\ O_3) \end{array}$$

But calculating the Fe PO_4 and the Al PO_4 separately to their respective oxide, there is found:—

$$\begin{array}{l} Fe\ PO_4 \quad 0.219 = 0.1160 \quad Fe_2\ O_3 \\ Al\ PO_4 \quad 0.054 = 0.0225 \quad Al_2\ O_3 \\ \left.\begin{array}{c} Fe\ PO_4 \\ + \\ Al\ PO_4 \end{array}\right\} 0.273 = 0.1385 \left\{\begin{array}{c} Fe_2\ O_3 \\ + \\ Al_2\ O_3 \end{array}\right. \end{array}$$

a higher result than obtained above.

If the composition of the same weight of the combined phosphates of iron and aluminium be assumed to consist of

$$\begin{array}{ll} Fe\ PO_4 & 0.054 \\ Al\ PO_4 & \underline{0.219} \\ & 0.273 \end{array}$$

there will result as before:—

$$\begin{array}{ccc} 0.273 & = & 0.131 \\ (Fe\ PO_4 + Al\ PO_4) & & (Fe_2\ O_3 + Al_2\ O_3) \end{array}$$

But,

$$\begin{array}{l} Fe\ PO_4 \quad 0.054 = 0.0286 \quad Fe_2\ O_3 \\ Al\ PO_4 \quad 0.219 = 0.0915 \quad Al_2\ O_3 \\ \left.\begin{array}{c} Fe\ PO_4 \\ + \\ Al\ PO_4 \end{array}\right\} 0.273 = 0.1201 \left\{\begin{array}{c} Fe_2\ O_3 \\ + \\ Al_2\ O_3 \end{array}\right. \end{array}$$

a value considerably lower than obtained by the other method of calculation.

Method II. makes a much better showing than the preceding method. The chief objection to it, is the error involved in weighing the iron and the aluminium as phosphates and calculating them to the oxides, as explained above.

This difficulty, however, could be obviated in the following manner:—

Proceed with the analysis exactly as directed, and weigh the iron and the aluminium as phosphates; then dissolve in $H_2\ SO_4$; reduce the iron by means of zinc and platinum in a $H_2\ SO_4$ solution; titrate with standardized $K_2\ Mn_2\ O_8$ solution, and record the iron as $Fe_2\ O_3$; calculate this to iron phosphate, Fe PO_4; subtract this value from the weight of the combined phosphates, and then calculate the remainder, the Al PO_4 to $Al_2\ O_3$.

Method III. has certainly yielded the most satisfactory result, for the difference between the amount of the iron and the aluminium oxides present and determined is only 0.04 per cent, a difference corresponding to less than two-tenths of a milligramme in the actual weight of the precipitate, $Fe_2\ O_3 + Al_2\ O_3$, in this experiment.

The feature which serves as the special endorsement of this method is the fact that the constituents sought are reported in the very form in which they are weighed, and that thus the introduction of errors by calculation is excluded.

In order to test the working of these three methods in actual practice they were applied to the analysis of four samples of bone black.

The results obtained follow:—

Sample.	Method I.	Method II.	Method III.
1	0.65	0.47	0.47
2	0.50	0.44	0.54
3	0.58	0.41	0.46
4	0.43	0.36	0.38

OSTEOLOGICAL NOTES.

BY DANIEL DENISON SLADE, M.C.Z., CAMBRIDGE, MASS.

THE jugal arch in the order of the Cetacea presents some singular modifications. In the Delphinoidea, the squamosal, frontal, and jugal enter into its composition. The squamosal sends forward a large, bulky process which nearly meets the descending post-orbital process of the frontal. The jugal is an irregular flat bone, covered by the maxilla, and sends back from its anterior and internal border a long and very slender process, curved slightly downwards, to articulate with the short, obtuse process of the squamosal, thereby forming the lower boundary of the orbit.

So far as the relations of the squamosal and jugal are concerned, the portion of the arch thus formed is a counterpart of that of the horse; although the union of the two bones is much more complete in the latter animal. The jugal in the horse is relatively a much larger bone, and sends back a well-developed process which underlies that of the squamosal, with which it is joined by a