

Notes

DISCREPANCIES OBSERVED IN THE COLORIMETRIC ESTIMATION OF SILICON IN HIDUMINIUM RR. SERIES OF ALUMINIUM ALLOYS

A METHOD for the estimation of silicon in aluminium alloys similar to that published by Hadley (*ANALYST*, 1941, **66**, 486; 1942, **67**, 9) has been developed and employed with success in our laboratories for many types of alloys.

In the main our results have agreed with those obtained by his method, but in several instances we have observed definite discrepancies between the gravimetric and colorimetric results on the same sample. In these determinations the gravimetric and the spectrographic results are considerably higher than the colorimetric result, as can be seen below. Each of the values quoted represents a mean of the results obtained by several different laboratories.

		Silicon, %		
		Chemical	Spectrographic	Colorimetric
Specimen No. 1	..	0.89	0.85	0.69
Specimen No. 2	..	1.18	—	1.03

The behaviour of two samples on prolonged boiling in the caustic soda soln. was further investigated. For the great majority of the numerous samples tested identical extinction values were obtained with boiling times of 5, 10 and 15 min.; slightly higher values were obtained with longer periods. The effect of boiling times was markedly different for "suspect" and "control" samples under identical conditions. Prolonged boiling of the suspect sample gives neither a consistent value of extinction, nor one in agreement with the gravimetric result. No explanation of this has yet been evolved. The possibility of such discrepancies, rare as they are, should be borne in mind in connection with the colorimetric estimation of silicon in aluminium alloys.

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ATTACK BY FUSION OF PYRITES AND CHROMITE

In the fusion of chromite with sodium peroxide in a nickel crucible, or of pyrites with sodium peroxide or a mixture of sodium peroxide and sodium carbonate, the metal is also attacked considerably and, if the crucible is worn or thin, its base may collapse. Further, when a Bunsen flame is used the products of combustion may contaminate the fused mass and introduce an error in a determination of sulphur in mineral sulphides.

These disadvantages are avoided easily by using a flux consisting of equal parts by weight of sodium hydroxide and sodium peroxide, which readily and completely attacks pyrites, chalcocite, bornite, and chromite at relatively low temperatures. Attack on the crucible is minimised and, for the sulphide minerals, an alcohol flame can be substituted for the Bunsen or the muffle, and contamination by extraneous sulphur avoided.

Procedures based on these considerations have been used here for the last 2 years for the minerals mentioned above, and have given good results even in inexperienced hands. The methods recommended are as follows:

PYRITES.—Place 3 g of sodium hydroxide and 3 g of sodium peroxide, both sulphur-free, in a nickel crucible (4 cm diam. at the mouth) fitted into asbestos board so that one-half of the crucible projects below. Weigh accurately on to the mixture 0.4–0.5 g of the powdered pyrites and mix thoroughly by means of a piece of stout copper wire. Cover the mixture evenly with 1 g of sodium peroxide, and heat slowly to fusion over a large-sized, methylated-spirit lamp, keeping the crucible covered. Maintain the mass in a fused condition for 15 min. by keeping the lower half of the crucible enveloped in the alcohol flame. When cold, extract the melt with water in a covered 400-ml beaker, dilute to approx. 200 ml, remove and rinse the crucible and lid. Boil for 5 min. to decompose excess peroxide, allow the solid matter to settle, and decant the supernatant liquid through an 11-cm., No. 540 Whatman paper into a 1-litre beaker. Add filter-paper pulp to the residue in the beaker, mix well, and complete the filtration. Wash thoroughly with 400 to 500 ml of hot 1% sodium carbonate soln. Boil, acidify the filtrate and washings, and determine the sulphate in the usual way.

CHROMITE.—Follow the same procedure as for pyrites, but omit covering the mixture of a sample and flux with a layer of sodium peroxide, and use a Bunsen flame for the heating. After fusion of the mass, heat the base of the crucible finally just to redness and keep at that temp. for 15 min. Extract the sodium chromate and determine it volumetrically. Extraction of chromium is complete.

When these fusions are made exactly as described the residues can be dissolved completely in the minimum quantity of dil. hydrochloric acid, no hydrogen sulphide is liberated from the pyrites residue, and no sulphate is detectable in the hydrochloric acid soln. Similarly, the soln. of the residue from the chromite gives a colourless filtrate when poured into an equal vol. of 10% sodium hydroxide soln. containing sodium peroxide, boiled and filtered. These checks should always be made to ensure that extraction of the sulphur or chromium is complete.

The use of a mixture of sodium peroxide and hydroxide as a means of attacking chromite is not new,¹ but its advantages appear to have been overlooked, and the method has never come into general use.² The procedures described above works so smoothly and well that the use of this flux merits revival, especially at a time when metal crucibles are difficult to obtain, and must be made to last as long as possible.

REFERENCES

1. For references see Mellor and Thompson, "*Quantitative Inorganic Analysis*," 1938, p. 528.
2. See, e.g., Treadwell and Hall, "*Analytical Chemistry*," Vol. II, 1935, pp. 327, 328, 451, 592, 593, 619; Hillebrand and Lundell, "*Applied Inorganic Analysis*," 1929, pp. 408, 573; Scott and Furman, "*Standard Methods of Chemical Analysis*," 1939, pp. 284, 285, 291, 295, 296, 297, 301, 302, 906.

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"PERSPEX" IN LABORATORY WORK

OCCASIONALLY a cell of a certain shape, or of special dimensions, is required for one of the various physico-chemical or physical methods used in the laboratory, and "Perspex" is admirably adapted for such purposes. For example, I have found in this artificial resin a suitable material for making the useful cell devised by C. A. Mitchell and T. J. Ward (ANALYST, 1933, 57, 760) to be fixed on the lens of a camera for certain types of photographic work. "Perspex," which chemically is a polymerised methyl methacrylate, has also been used to make cells of various dimensions to hold liquid colour filters, liquids to eliminate ultra-violet light but pass all visible light, as in "fluorescence photography," and the cells used in the Spekker Absorptiometer and in the spectrophotometer. It has also been employed commercially in the manufacture of lenses and prisms and the absorbing filters used in photo-engraving and photo printing. Again, it has been found that where a negative has to be projected on to a screen for a long period, as with backgrounds in cinema studios, "Perspex" is a much better support than glass, as the latter becomes heated very rapidly when transmitting light from the carbon arc and this seriously affects the negative, whereas "Perspex" remains relatively cool. This resin is at present controlled by the Plastic Controller and it will be available in limited quantities for work of national importance only, but a study of a few of its properties set out below may suggest a number of uses in the post-war period.

The material is produced in sheet form and is characterised by its absence of colour, high refractive index and very pronounced transparency. Its water absorption after 24 hr. is approx. 0.4% and its thermal expansion is 97.5×10^{-6} per 1°C . It softens at about 120°C . and sheets heated in front of a radiator or in an oven until soft will readily take impressions or can be moulded round curved objects. In forensic work, for example, when a coin and "Perspex" sheet are heated until the resin is soft and the coin is pressed on and held by a heavy weight until quite cold, a permanent impression showing all the minute details or flaws on the face of the coin is thus obtained in a few minutes. When the impression has served its purpose the resin is heated until just soft, when it regains its original flat surface; this procedure may be repeated a number of times.

As lines may be readily engraved on the material with a sharp steel needle, sheets ruled in squares are readily prepared suitable for use in photographing typescript and handwriting when documents are being examined. The resin can be drilled with an ordinary hand drill, cut with a hacksaw and joined with "Perspex" cement or a soln. of polymethyl methacrylate in a solvent such as chloroform. It is unattacked by 10% nitric acid during 14 days at room temp., or by 31% hydrochloric acid or 20% sulphuric acid after the same length of time, either at room temp. or at 60°C . Most salt solutions have no effect on the resin, which will withstand a saturated soln. of sodium hypochlorite. It is unaffected by many organic solvents, but other organic liquids may cause it to become cloudy or to dissolve. Space does not allow a list to be given of the effects of various organic liquids, but this information can, no doubt, be supplied by the makers.

The refractive index of the material varies according to the amount of plasticiser present. Unplasticised "Perspex" of optical quality has a n_D , 1.4896, that of the normal commercial quality being 1.4949. Graphs made by the makers have shown the valuable optical properties of "Perspex" in both the ultra-violet and infra-red spectral regions. To obtain solid, optically-clear colour filters the material can be dyed to any shade required, and I have found this dyed material to be of use in forensic work in which the normal colour filters are usually employed. Many other uses will suggest themselves from a study of the properties of the resin given by the manufacturers.

My thanks are due to I.C.I. (Plastics), Ltd., who have supplied me with samples of "Perspex," and have given me a number of the details mentioned above, and to the Directors of I.C.I. (Dyestuffs), Ltd., for permission to publish this note.

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