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A CONVENIENT METHOD FOR THE ANALYSIS OF ORGANOMETALLIC AND RELATED COMPOUNDS

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Summary

X-ray spectrometry of small amounts of compounds presented as pressed discs in borax is shown to be a convenient method for analysis, and is especially suitable for compounds which are not amenable to conventional combustion analyses.

The difficulty of achieving sufficiently high temperatures for satisfactory carbon, hydrogen and nitrogen analyses of compounds containing both a metallic element and a second row main group element, for example sulphur, prompts us to draw attention to a convenient method we have developed for the X-ray spectrometric analysis of such compounds.

X-ray fluorescence spectrometry is a well-established technique for elemental analysis. Samples are usually presented as massive solids, powders or pressed discs, or in diluted form as solutions, or as annealed melts in some suitable substrate. When only a small amount of material is available some form of dilution is desirable to produce a sample of the right dimensions for the spectrometer. Liquid solutions, although ideally homogeneous, are not suitable for light element analysis since the longer wavelengths emitted from such elements are absorbed by the liquid cell window. The use of annealed melts is precluded if loss of material occurs on heating.

We have found that small amounts of sample dispersed in KCl or borax and pressed into discs under constant pressure are in a convenient form for quantitative analysis. The use of KCl discs is restricted to 'heavy' element analysis ($Z > 25$) whilst borax discs may be used for all elements above $Z = 13$. Calibration graphs are obtained by use of known, independently analysed compounds containing the desired elements in a generally similar chemical environment.

The product and residues from the reaction of analytically pure tetramethylammonium thiocyanate with chlorotris(triphenylphosphine)rhodium(I) in acetonitrile have been analysed by these methods. It has been possible to account for all the rhodium, phosphorus, chlorine and sulphur used. Thus, the product [1] of the reaction has been identified as $Rh(PPh_3)_2(CH_3CN)(SCN)$, whereas attempts to characterise the same compound from C, H and N analyses, obtained by combustion, are generally unsatisfactory for this and other *S*-bonded rhodium compounds. On the other hand, the closely related *N*-bonded compounds [e.g. the known [2] $Rh(CO)(PPh_3)_2(NCS)$] may be characterised adequately by either method.

Generally in the compounds we have examined, rhodium, iridium, selenium and tellurium analyses expressed as a percentage by weight are accurate to within 0.1%, and phosphorus, sulphur and chlorine analyses to within 0.3%.

Experimental

The analyses were made using a Philips PW1540 vacuum spectrograph attachment with a wide range goniometer PW1050. For light element conditions a penta-erythritol analysing crystal was used together with a gas-flow (90% Ar, 10% CH_4) proportional counter. The argon/methane gas was passed through pyrogallol and concentrated sulphuric acid to remove traces of oxygen and water. For heavy element analysis a LiF (100) crystal was used with a NaI(Tl) scintillation counter. The pulses from either detector were fed via a pulse-height analyser to a ratemeter/scaler unit. Heavy elements may be analysed under light element conditions if an emission of suitable energy exists, e.g. the $L\alpha$ line of rhodium.

A typical disc [e.g. for $Rh(PPh_3)_2(MeCN)(SCN)$] requires 50 - 100 mg of sample pressed with 1.0 g of borax at 30 tons for 10 minutes.

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References

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