

- 7 Y. Ning, F. Wen, H. Zhao and D. Deng, *Rare Metals*, 1994, **13**, (2), 143
- 8 M. P. Slavinskyi, *Physico-Chemical Properties of Elements*, Metallurgizdat, Moscow, 1952, (in Russian)
- 9 R. Hultgren, P. G. Desai and D. T. Hawkins, in "Selected Values of the Thermodynamic Properties of Elements", American Society for Metals, Metals Park, Ohio, 1973
- 10 K. S. Kim, A. F. Gossmann and N. Winograd, *Anal. Chem.*, 1974, **46**, (1), 197
- 11 F. M. John, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Physical Electronic Division, U.S.A., 1992
- 12 J. C. Chaston, *Platinum Metals Rev.*, 1965, **9**, (4), 126
- 13 Y. Ning, Z. Yang and H. Zhao, *Platinum Metals Rev.*, 1995, **39**, (1), 19
- 14 Z. Yang, Y. Ning and H. Zhao, *J. Alloys Compd.*, 1995, **218**, 51

## Iridium Apparatus for XRF Fusions

The properties required of containment materials used for X-ray fluorescence analysis (XRF) applications include good chemical resistance to the borate fluxes commonly used in the preparation of samples, sufficient hot strength to give an acceptable service life, and good wetting resistance. It must also be possible to work the material into the required form. Therefore, platinum, gold-platinum and gold-rhodium-platinum were widely used for this purpose, and the good surface finish on sample beads produced in ZGS 5 per cent gold-platinum casting moulds resulted in improved analytical accuracy (*Platinum Metals Rev.*, 1982, **26**, (3), 98).

Even these materials can be damaged, however, by the fusion of certain matrices, including some sulphides and unoxidised base metals. Now a paper from the Geoservices Centre of the Ministry of Northern Development and Mines, Canada, describes preliminary tests made to find if iridium could be used for the fusion

of specific samples for XRF analysis (A. Martin, in "Summary of Field Work and Other Activities", 1995, Ontario Geological Survey, Miscellaneous Paper, 164, pp. 233-236).

The samples tested contained unoxidised base metals, sulphides, carbides and arsenides. Although the iridium crucibles contained manufacturing flaws, they did survive the fusion processes. Experiments were also performed to determine if iridium suffered from the "memory effect", where elements present in one melt would enter into the containment material and be released into subsequent samples. While iridium possesses wetting properties, it showed little or no loss of surface integrity during these metal permeability tests.

Thus, analytical sample beads have been produced in iridium crucibles from materials that would have significantly damaged and contaminated platinum apparatus. Further tests are to be carried out on new flaw-free iridium crucibles and the results are awaited with interest.

## Ruthenium/Platinum in Water Electrooxidation

The oxidation of water is a basic reaction in photosynthesis, and for artificial photosynthesis any improvements to water oxidation systems must be welcome. Various systems can produce oxygen from water using metal oxides, RuO<sub>2</sub>, IrO<sub>2</sub>, PtO<sub>2</sub>, and heterogeneous and homogeneous systems with metal complexes acting as the molecule-based catalyst. The trinuclear ruthenium complex, [(NH<sub>3</sub>)<sub>5</sub>Ru-O-Ru(NH<sub>3</sub>)<sub>4</sub>-O-Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>6+</sup> (Ru-red) is one of the most active molecule-based catalysts. However, such catalysts have inefficient charge transfer between the electrode and the metal complex.

Researchers from Ibaraki University, Mito and the Institute of Physical and Chemical Research, Wako, Japan, have now designed a very active catalyst system for electrochemical water oxidation (M. Yagi, I. Ogino, A. Miura, Y. Kurimura and M. Kaneko, *Chem. Lett. Jpn.*, 1995, (10), 863-864). Ru-red was adsorbed onto platinum black (Pt-black) electrodeposited

onto the surface of a basal-plane pyrolytic graphite (BPG) electrode, and electrochemical water oxidation tests were performed. The BPG/Pt-black [Ru-red] displayed an exceptionally steep rise in anodic current for oxygen evolution above 1.2 V. The current size after one hour at 1.3 V was 7.4 mA/cm<sup>2</sup>, almost 10 times that for a BPG/Pt-black electrode. Additionally, oxygen began to evolve at 150 mV lower than for BPG/Pt-black, and the maximum oxygen evolution occurred when the ratio of Pt-black:Ru-red was 6.0 × 10<sup>-3</sup>:9.3 × 10<sup>-3</sup>.

The high activity of the system is ascribed to each Ru-red molecule oxidising water in a 4-electron oxidation, as long as the trinuclear structure of the ruthenium red complex is maintained. The electrode matrix also strongly affects the activity of the Ru-red. When adsorbed on the Pt-black surface, charge is directly and efficiently injected from the Pt-black to the Ru-red complex; accounting for the high catalytic activity.