Platinum Group Metals Technology

Gmelin Handbook of Inorganic Chemistry, 8th Edition, Platinum, Suppl. Vol. A 1
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History records that in 1822 Leopold Gmelin (1788–1853), then Professor of Chemistry at Heidelberg University made a modest contribution to the advancement of the chemistry of the platinum metals by his discovery, in collaboration with Fredrich Wöhler, of the double potassium cyanides of both platinum and palladium. A more notable and lasting achievement was, of course, the establishment in 1817 of his "Handbook of Theoretical Chemistry" which recorded and reviewed progress in that subject. Over the intervening years this process has continued, and although organic chemistry is no longer included the length and importance of the publication has grown remarkably as has the task of compiling it. Now the responsibility of the Gmelin Institute for Inorganic Chemistry, one of the institutes of the Max-Planck Society for the Advancement of Science, the handbook is currently in its 8th edition.

The recently available Gmelin volume on the technology of the platinum group metals has been written by an international team, each member of which is a recognised authority on their specialised topic. First the recovery of the platinum group metals is considered by R. I. Edwards, W. A. M. te Riele and G. J. Bernfeld, of the Council for Mineral Technology, Randburg. In a 23 page chapter the established methods of concentrating and refining the platinum group metals are considered, as are the most modern extraction techniques.

The purity of the platinum metals has long been important to people investigating the structure and properties of these metals, but increasingly their successful application under arduous conditions in high-technology fields is dependent, to a very large extent, upon the absence of impurities. The chapter on high purity metals, prepared by W. Westwood, formerly of Johnson Matthey, occupies 42 pages and complements the preceding chapter by first considering the methods used to refine the metals. It then goes on to review the various purification routes and the methods of determining impurities.

Although the electrodeposition of platinum has been practised for over 150 years, the subject still attracts considerable interest as users strive to exploit the properties of certain of the platinum group metals in the most economical way. Within the 26 pages devoted to electrodeposition, ruthenium, palladium, osmium, iridium and platinum have been reviewed by Ch. J. Raub, of Forschungsinstitut für Edelmetalle und Metallchemie, and rhodium by F. Simon of Degussa. The properties of electrodeposited rhodium, which include tarnish resistance, good wear resistance, low contact resistance, high reflectivity and attractive colour, make it a most useful material for both industrial and decorative purposes. Iridium plating has not found wide technical application due to practical difficulties, while a lack of interest has, perhaps, restricted the investigation of osmium deposits. Despite extensive investigation, electrodeposited ruthenium has found only limited industrial application. Within the electronics industry there is an economic incentive to use palladium electrodeposits as a substitute for gold. There is little interest in platinum for this particular purpose, but it finds application elsewhere and the various methods of coating substrates with platinum are considered.

In view of their long established use for many important industrial applications it is not surprising that the chapter devoted to platinum group metals, alloys and compounds in catalysis forms, by far, the largest part of this volume. Within these 226 pages, prepared by A. J. Bird of the Johnson Matthey Technology Centre, all major aspects of platinum group metals catalyst chemistry and technology are

Other Gmelin Volumes on the Platinum Group Metals		
*Platinum A 1:	History, Occurrence	1938
*Platinum A 2:	Occurrence	1939
*Platinum A 3:	Preparation of Platinum Metals	1939
*Platinum A 4:	Detection and Determination of the Platinum Metals	1940
*Platinum A 5:	Alloys of Platinum Metals : Ru, Rh, Pd	1949
*Platinum A 6:	Alloys of Platinum Metals : Os, Ir, Pt	1951
*Platinum B 1 :	Physical Properties of the Metal	1939
*Platinum B 2 :	Physical Properties of the Metal	1939
*Platinum B 3 :	Electrochemical Behaviour of the Metal	1939
*Platinum B 4 :	Electrochemical Behaviour and Chemical Reactions	1942
*Platinum C 1 :	Compounds up to Platinum and Bismuth	1939
*Platinum C 2 :	Compounds up to Platinum and Caesium	1940
*Platinum C 3 :	Compounds up to Platinum and Iridium	1940
*Platinum D :	Complex Compounds of Platinum with Neutral Ligands	1957
*Palladium 1 :	Element	1941
*Palladium 2 :	Compounds	1942
*Rhodium :	Main Volume	1938
Rhodium :	Suppl.Vol.B 1 : Compounds	1982
Rhodium :	Suppl.Vol.B 2 : Co-ordination Compounds	1984
Rhodium :	Suppl.Vol.B 3 : Co-ordination Compounds	1984
*Iridium :	Main Volume	1939
*Iridium :	Suppl.Vol.1 : Metal, Alloys	1978
**Iridium :	Suppl.Vol.2 : Compounds	1978
*Osmium :	Main Volume	1939
Osmium :	Suppl.Vol.1	1980
*Ruthenium :	Main Volume	1938
*Ruthenium :	Suppl.Vol.	1970
Platinum :	Suppl.Vol.A 2 : Isotopes, Atoms, Molecules and Clusters of Platinum Metal Elements	1989
Palladium :	Suppl.Vol.B 2 : Compounds	1989
Palladium :	Suppl.Vol.B 1 : Palladium-Hydrogen Compounds	1990
Osmium :	Organo Osmium Compounds	1990

* Completely or ** partially in German, otherwise in English

reviewed; indeed it seems unlikely that any significant topic has been neglected. Major divisions include 55 pages on unsupported metals and metal alloy catalysts and 23 pages on supported metals and metal alloy catalysts, while platinum group metal compounds in catalysis occupies 122 pages. These three are then subdivided into sections on preparation, properties and the various reactions for which they are used. Although there is no index within the volume, the table of contents and the general arrangement of this and other chapters, enables readers to locate readily the sections of particular interest.

The biological activity of platinum compounds and their medical uses is considered by

P. Köpf-Maier of the University of Ulm and H. Köpf of the Technische Universität, Berlin. In contrast to the preceding tome, this 23 page section is concerned with knowledge which has been accumulated during a period of only about twenty years. The progress made in this time is remarkable, and one may anticipate that a later Gmelin supplement will have to devote a more lengthy section to this important topic.

In the main, this handbook covers the literature up until 1983, and its importance results from the many relevant sources referenced. These also serve to indicate the publications that should be searched by investigators requiring more recent information. At the front of this book a list is given of other Gmelin volumes on the platinum group metals. These are likely to emphasise work regarded as particularly significant up to the time of their publication, and they are tabulated here for the benefit of readers who may wish to study other aspects of platinum group metals chemistry.

Determining the Freshness of Fish

There is an obvious requirement that food for human consumption should be fit for the intended purpose, and producers, processors and distributors all have considerable responsibility for this. In Japan fish form a particularly important part of the diet, and there is therefore a special interest in ensuring that their quality can be monitored accurately. During the past year two communications from researchers in the Department of Materials Science and Engineering, at Nagasaki University, have reported the development of a sensor capable of determining the freshness of fish (1, 2).

Fish freshness can be expressed by the K value, this being defined as the percentage of inosine and hypoxanthine present among the adenosine triphosphate related compounds in fish muscle. However, the process of determining this data is destructive, and requires considerable time and effort.

After death the quality of fish deteriorates, and as it does gaseous species are given off including trimethylamine, the concentration of which increases significantly as the freshness decreases. Thus there is a possibility of determining the freshness of fish by monitoring changes in the concentration of emitted trimethylamine, and this led the Nagasaki University team to develop semiconductor gas sensors that were highly sensitive to trimethylamine. Initially stannic oxide, a typical semiconductive metal oxide, was employed, either on its own or with additions of palladium, ruthenium or gold. This sensor material was applied to the outer surface of an alumina tube on which two gold electrodes were printed, and which could be heated to a given temperature by means of a small nichrome coil inserted in the tube. Gas sensitivity, defined as the ratio of the electrical resistance of the sensor in dry air to that in a sample gas, was measured in a flow apparatus. Of the sensor materials studied the one containing ruthenium was found to be the most sensitive to 300ppm of trimethylamine, at a temperature of about 555°C.

Subsequent work to develop more sensitive sensor materials involved zinc oxide, tungsten oxide and titanium oxide, both on their own and with the addition of 0.5 weight per cent ruthenium. The maximum sensitivity to 300ppm trimethylamine in a sample gas was exhibited by the titania element containing ruthenium.

Following this finding the investigators went on to demonstrate the suitability of this element for monitoring the freshness of the fish known as Japanese saurel. The electrical resistance changes of the sensor element, held at a temperature of 555°C, continuously monitored the condition of the fish which was stored in a closed box at room temperature, while gas chromatography confirmed that trimethylamine was among the gaseous species emitted. For comparative purposes the K value of similar fish stored under the same conditions was determined by analysis of the adenosine triphosphate related compounds in the fish muscle. This interesting work confirmed that resistance changes of a ruthenium/titania sensor element could sensitively and selectively detect trimethylamine, thus demonstrating the potential of this method for rapidly and non-destructively monitoring fish freshness.

References

1 M. Egashira, Y. Shimizu and Y. Takao, *Chem. Lett. Jpn.*, 1988, (3), 389

2 M. Egashira, Y. Shimizu and Y. Takao, *J. Electrochem. Soc.*, 1988, **135**, (10), 2539