

The Discoverers of the Iridium Isotopes

THE THIRTY-SIX KNOWN IRIDIUM ISOTOPES FOUND BETWEEN 1934 AND 2001

By J. W. Arblaster

Coleshill Laboratories, Gorsey Lane, Coleshill, West Midlands B46 1JU, U.K.

This paper is the second in a series of reviews of work performed that led up to the discoveries of the isotopes of the six platinum group elements. The first review, on platinum isotopes, was published in this Journal in October 2000 (1). Here, a brief history of the discovery of the thirty-six known isotopes of iridium in the sixty-seven years from the first discovery in 1934 to 2001 is considered in terms of the discoverers.

Of the thirty-six isotopes of iridium known today, only two occur naturally with the following authorised isotopic abundances (2):

The Naturally Occurring Isotopes of Iridium	
Mass number	Isotopic abundance, %
^{191}Ir	37.3
^{193}Ir	62.7

Although Arthur J. Dempster (3) is credited with the discovery of these two isotopes at the University of Chicago, Illinois, in late 1935, using a new type of mass spectrograph that he had developed; earlier that year Venkatesachar and Sibaiya (4) of the Department of Physics, Central College, Bangalore, India, had observed isotopic shifts in the hyperfine arc spectrum of iridium which they suggested were due to masses 191 and 193 in the approximate ratio of 1:2. At that time, this seemed to be incorrect as it resulted in an atomic weight for iridium of 192.4 which was much lower than the then accepted value of 193.1 (5). However, in 1936, Sampson and Bleakney (6) carried out a precision determination of the isotopic ratio using a mass spectrograph. This confirmed the above approximate ratio and eventually, in 1953, the atomic weight was lowered to 192.2 (7).

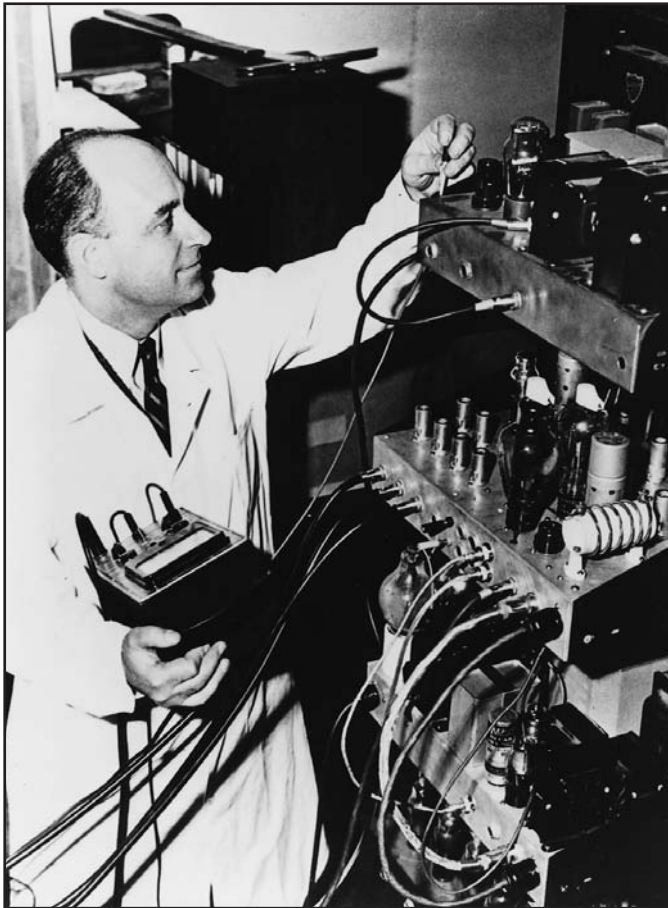
Artificial Iridium Isotopes

Almost immediately after the published discovery of artificial radioactivity by Curie and Joliot in 1934 (8), Fermi and colleagues of the Physics

Laboratory, University of Rome, identified a 20 hour activity (activity is generally used to indicate the half-life of a non-specified isotope) after bombarding iridium with slow neutrons (9).

In 1935, the same group (10) refined the half-life to 19 hours, although Sosnowski (11) was unable to confirm this period but instead obtained activities of 50 minutes and three days for the half-lives. In 1936, Amaldi and Fermi (12) also discovered an activity which they assigned to iridium, but its half-life was 60 days. In the same year Cork and Lawrence (13) bombarded platinum with deuterons (deuterium ions) and obtained activities with half-lives of 28 minutes and 8.5 hours which they claimed were definitely associated with iridium following chemical identification. In 1937 Pool, Cork and Thornton (14) bombarded iridium with neutrons and obtained a 15 hour activity which was very similar to that obtained by Fermi and colleagues back in 1934.

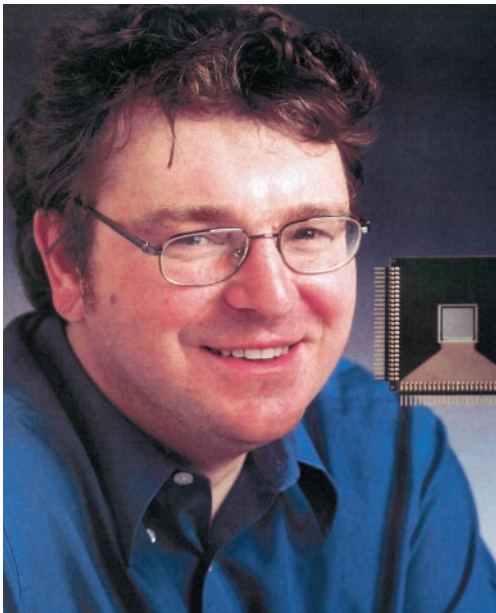
However, although in 1935 Dempster (3) had identified the naturally occurring isotopes, and the various radioactive discoveries could probably be assigned to the missing ^{192}Ir , ^{194}Ir or ^{195}Ir , Livingston and Bethe (15), in a review in 1937, concluded that the situation was confused and that no firm mass assignments could be given at that time. However, in the same year McMillan, Kamen and Ruben of the Department of Physics and Chemistry at the University of California (16) confirmed the 19 hour activity of Fermi and colleagues (9, 10) and correctly assigned it to ^{194}Ir while they also confirmed the 60 day activity of Amaldi and Fermi (12) which they assigned to ^{192}Ir . Actually



Enrico Fermi
1901–1954

The physicist Enrico Fermi was born in Rome, Italy. In 1926 Fermi discovered the statistical laws governing the behaviour of particles of quantum spin one half, which are now known as fermions. A year later he became Professor of Theoretical Physics at the University of Rome where he evolved the theory of beta decay. In 1934 he set up the group which led to the discovery of numerous artificial radioactive isotopes obtained by bombarding elements with neutrons and for this he received the 1938 Nobel Prize in Physics. Immediately afterwards he moved to the United States, first to Columbia University, then to the University of Chicago to be Professor of Nuclear Studies. He was a leading member of the team that produced, on 2nd December 1942, the first controlled nuclear chain reaction. After the war he concentrated on high energy physics and cosmic rays. Element 100 is named fermium in his honour

University of Chicago, courtesy of AIP Emilio Segrè Visual Archives



Philip John Woods

Professor of Nuclear Physics at the University of Edinburgh. Philip Woods is a spokesman of a British-American collaboration that has performed experiments at the Argonne National Laboratory, Chicago, resulting in the discovery and measurement of a large number of proton-emitting isotopes. These include the four most unstable iridium isotopes from ^{164}Ir to ^{167}Ir . The object to the right of Philip Woods is the pioneering double-sided silicon strip detector (DSSD) used to identify iridium isotopes by their radioactive decays

The Discoverers of the Iridium Isotopes

Mass number	Half-life	Decay modes	Year of discovery*	Discoverers	Ref.	Notes
164m	100 μ s	p	2000	1: Kettunen <i>et al.</i> 2: Mahmud <i>et al.</i>	22 23	A
165m	300 μ s	p, α	1995	Davids <i>et al.</i>	20, 21	
166	10.5 ms	α , p	1995	Davids <i>et al.</i>	20, 21	
166m	15.1 ms	α , p	1981	Hofmann <i>et al.</i>	25	B
167	35.2 ms	α , p, EC + β^+	1995	Davids <i>et al.</i>	20, 21	
167m	30.0 ms	α , EC + β^+ ?, p	1981	Hofmann <i>et al.</i>	25	C
168	125 ms	α ?, EC + β^+ ?	1978	Cabot <i>et al.</i>	27	D
168m	161 ms	α	1995	Page <i>et al.</i>	26	
169	780 ms	α , EC + β^+ ?	1999	Poli <i>et al.</i>	28	E
169m	310 ms	α , EC + β^+	1978	1: Cabot <i>et al.</i> 2: Schrewe <i>et al.</i>	27 29	F
170	870 ms	EC + β^+ , α	1995	Page <i>et al.</i>	26	G
170m	440 ms	EC + β^+ , IT, α	1977	1: Cabot <i>et al.</i> 2: Schrewe <i>et al.</i>	31 29	H
171	3.2 s	α , EC + β^+ , p?	2001	Rowe <i>et al.</i>	32	
171m	1.40 s	α , EC + β^+ , p?	1966	Siivola	19	I
172	4.4 s	EC + β^+ , α	1991	Schmidt-Ott <i>et al.</i>	34, 35	
172m	2.0 s	EC + β^+ , α	1966	Siivola	19	J
173	9.0 s	EC + β^+ , α	1991	1: Bouldjedri <i>et al.</i> 2: Schmidt-Ott <i>et al.</i>	36 34, 35	
173m	2.20 s	EC + β^+ , α	1966	Siivola	19	K
174	9 s	EC + β^+ , α	1991	1: Bouldjedri <i>et al.</i> 2: Schmidt-Ott <i>et al.</i>	36 34, 35	
174m	4.9 s	EC + β^+ , α	1966	Siivola	19	L
175	9 s	EC + β^+ , α	1966	Siivola	19	
176	8 s	EC + β^+ , α	1966	Siivola	19	
177	30 s	EC + β^+ , α	1966	Siivola	19	
178	12 s	EC + β^+	1970	Akhmadzhanov <i>et al.</i>	37, 38	
179	1.32 min	EC + β^+	1971	Nadzhakov <i>et al.</i>	39	M
180	1.5 min	EC + β^+	1970	1: Akhmadzhanov <i>et al.</i> 2: Nadzhakov <i>et al.</i>	37, 38 39	
181	4.90 min	EC + β^+	1970	1: Akhmadzhanov <i>et al.</i> 2: Nadzhakov <i>et al.</i>	37, 38 39	
182	15 min	EC + β^+	1961	Diamond <i>et al.</i>	40	
183	58 min	EC + β^+	1960	1: Lavrukhina, Malysheva and Khotin 2: Diamond <i>et al.</i>	41 40	
184	3.09 h	EC + β^+	1960	1: Baranov <i>et al.</i> 2: Diamond <i>et al.</i>	42 40	
185	14.4 h	EC + β^+	1958	Diamond and Hollander	43	
186	16.64 h	EC + β^+	1957	Scharff-Goldhaber <i>et al.</i>	44	N
186m	1.92 h	EC + β^+ , IT?	1962	Bonch-Osmolovskaya <i>et al.</i>	46	
187	10.5 h	EC + β^+	1958	Diamond and Hollander	43	
187m	30.03 ms	IT	1962	Ramaev, Gritsyna and Korda	47	
188	41.5 h	EC + β^+	1950	Chu	48	
188m	4.2 ms	IT, EC + β^+	1970	Goncharov <i>et al.</i>	49	
189	13.2 d	EC	1955	Smith and Hollander	45	
189m1	13.3 ms	IT	1962	Ramaev, Gritsyna and Korda	47	
189m2	3.7 ms	IT	1974	1: André <i>et al.</i> 2: Kemnitz <i>et al.</i>	50 51	

* The year of discovery is taken as available manuscript and conference dates. Where these are not available then the year of discovery is the publishing date

The Discoverers of the Iridium Isotopes (<i>cont.</i>)						
Mass number	Half-life	Decay modes	Year of discovery*	Discoverers	Ref.	Notes
190	11.78 d	EC + β^+	1946	Goodman and Pool	52	
190m1	1.120 h	IT	1964	Harmatz and Handley	53	
190m2	3.087 h	EC + β^+ , IT	1950	Chu	48	
191	Stable	–	1935	Dempster	3	
191m	4.94 s	IT	1954	1: Butement and Poë	54	
				2: Mihelich, McKeown and Goldhaber	55	
				3: Naumann and Gerhart	56	
192	78.831 d	β^- , EC	1937	McMillan, Kamen and Ruben	16	O
192m1	1.45 min	IT, β^-	1947	Goldhaber, Muehlhouse and Turkel	57	P
192m2	241 y	IT	1959	Scharff-Goldhaber and McKeown	58	Q
193	Stable	–	1935	Dempster	3	
193m	10.53 d	IT	1956	Boehm and Marmier	60	
194	19.28 h	β^-	1937	McMillan, Kamen and Ruben	16	R
194m1	31.85 ms	IT	1959	Campbell and Fettweiss	61	
194m2	171 d	β^-	1968	Sunjar, Scharff-Goldhaber and McKeown	62	S
195	2.5 h	β^-	1952	Christian, Mitchell and Martin	65	
195m	3.8 h	β^- , IT	1967	Hofstetter and Daly	66	
196	52 s	β^-	1966	Venach, Münzer and Hille	67	T
196m	1.40 h	β^- , IT?	1966	Jansen and Pauw	69	U
197	5.8 min	β^-	1952	Christian, Mitchell and Martin	65	V
197m	8.9 min	β^- , IT?	1976	Petry <i>et al.</i>	72, 73	W
198	8 s	β^-	1972	Schweden and Kaffrell	74	X
199	(20 s)	β^-	1992	Zhao <i>et al.</i>	76	Y

Notes to the Table		
A	^{164m}Ir	Mahmud <i>et al.</i> (23) considered that the nuclide observed was an isomeric state not the ground state. The half-life is a weighted average of 113^{+62}_{-30} μs determined by Kettunen <i>et al.</i> (22) and 58^{+46}_{-18} μs determined by Mahmud <i>et al.</i> (23).
B	^{166m}Ir	Only the alpha energy was measured. The half-life was determined by Page <i>et al.</i> in 1995 (26) while the isomeric state assignment was by Davids <i>et al.</i> (21).
C	^{167m}Ir	Only the alpha energy was measured. The half-life was determined by Page <i>et al.</i> in 1995 (26) while the isomeric state assignment was by Davids <i>et al.</i> (21).
D	^{168}Ir	Only the alpha energy was measured. The half-life was determined by Page <i>et al.</i> in 1995 (26).
E	^{169}Ir	The half-life was normalised from 638^{+462}_{-237} ms determined by Poli <i>et al.</i> in 1999 (28).
F	^{169m}Ir	The isomeric state assignment was by Poli <i>et al.</i> (28). The half-life is a weighted average of 308 ± 22 ms determined by Page <i>et al.</i> (26) and 323^{+90}_{-60} ms by Poli <i>et al.</i> (28).
G	^{170}Ir	The half-life was selected by Baglin (30).
H	^{170m}Ir	The isomeric state assignment was by Page <i>et al.</i> (26). The half-life was selected by Baglin (30).
I	^{171m}Ir	The half-life was selected by Baglin (33) who also assigned the activity to be an isomeric state.
J	^{172m}Ir	The isomeric state assignment was by Schmidt-Ott <i>et al.</i> (34).

* The year of discovery is taken as available manuscript and conference dates. Where these are not available then the year of discovery is the publishing date

Notes to the Table (*cont.*)

K	$^{173\text{m}}\text{Ir}$	The isomeric state assignment was by Schmidt-Ott <i>et al.</i> (34).
L	$^{174\text{m}}\text{Ir}$	The isomeric state assignment was by Schmidt-Ott <i>et al.</i> (34).
M	^{179}Ir	Half-lives determined by Nadzhakov <i>et al.</i> (39) appear to be systematically in error but the discovery is otherwise accepted.
N	^{186}Ir	The isotope was actually discovered by Smith and Hollander in 1955 (45) but was wrongly assigned to ^{187}Ir .
O	^{192}Ir	The isotope was first observed as a non-specific activity by Amaldi and Fermi in 1936 (12).
P	$^{192\text{m1}}\text{Ir}$	The isotope was actually discovered by McMillan, Kamen and Ruben in 1937 (16) but was wrongly assigned to ^{194}Ir .
Q	$^{192\text{m2}}\text{Ir}$	Scharff-Goldhaber and McKeown only determined the half-life to be greater than five years. The accepted value was determined by Harbottle in 1969 (59).
R	^{194}Ir	The isotope was first observed as a non-specific activity by Fermi <i>et al.</i> in 1934 (9) and Amaldi <i>et al.</i> in 1935 (10).
S	$^{194\text{m2}}\text{Ir}$	A 47 s activity described as being an isomer of ^{194}Ir by Hennies and Flammersfeld in 1959 (63) could not be found by Scharff-Goldhaber and McKeown (64).
T	^{196}Ir	The isotope was first observed by Butement and Poë in 1953 (68) but was wrongly assigned to ^{198}Ir .
U	$^{196\text{m}}\text{Ir}$	Jansen and Pauw (69) suggested that the 20 h activity originally assigned to $^{196\text{m}}\text{Ir}$ by Bishop in 1964 (70) was actually a mixture of $^{196\text{m}}\text{Ir}$ and ^{195}Ir .
V	^{197}Ir	The 5.8 min half-life isotope was assigned to the ground state by Petry <i>et al.</i> in 1978 (71).
W	$^{197\text{m}}\text{Ir}$	The 8.9 min half-life isotope was assigned to be the isomeric state by Petry <i>et al.</i> in 1978 (71).
X	^{198}Ir	Details of this isotope were first given in the open literature by Szaley and Uray in 1973 (75).
Y	^{199}Ir	Only the mass of the isotope was determined. The half-life and decay mode were estimated from nuclear systematics (24).

Decay Modes

α	Alpha decay is the emittance of alpha particles which are ^4He nuclei. Thus the atomic number of the daughter nuclide is lower by two and the mass number is lower by four.
β^-	Beta or electron decay for neutron-rich nuclides is the emittance of an electron (and an anti-neutrino) as a neutron decays to a proton. The mass number of the daughter nucleus remains the same but the atomic number increases by one.
β^+	Beta or positron decay for neutron-deficient nuclides is the emittance of a positron (and a neutrino) as a proton decays to a neutron. The mass number of the daughter nucleus remains the same but the atomic number decreases by one. However, this decay mode cannot occur unless the decay energy exceeds 1.022 MeV (twice the electron mass in energy units). Positron decay is always associated with orbital electron capture (EC).
EC	Orbital electron capture. The nucleus captures an extranuclear (orbital) electron which reacts with a proton to form a neutron and a neutrino, so that, as with positron decay, the mass number of the daughter nucleus remains the same but the atomic number decreases by one.
IT	Isomeric transition, in which a high energy state of a nuclide (isomeric state or isomer) usually decays by cascade emission of γ (gamma) rays (the highest energy form of electromagnetic radiation) to lower energy levels until the ground state is reached. However, certain low level states may also decay independently to other nuclides.
p	The emittance of protons by highly neutron-deficient nuclides. As the neutron:proton ratio decreases a point is reached where there is insufficient binding energy for the last proton which is therefore unbound and is emitted. The point at which this occurs is known as the proton drip line and such nuclides are said to be "particle unstable".

Appendix

Some of the Terms Used for this Review

Atomic number	the number of protons in the nucleus
Mass number	the combined number of protons and neutrons in the nucleus
Nuclide and isotope	A nuclide is an entity characterised by the number of protons and neutrons in the nucleus. For nuclides of the same element the number of protons remains the same but the number of neutrons may vary. Such nuclides are known collectively as the isotopes of the element. Although the term isotope implies plurality it is sometimes used loosely in place of nuclide.
Half-life	the time taken for the activity of a radioactive nuclide to fall to half its previous value
Electron volt (eV)	The energy acquired by any charged particle carrying a unit (electronic) charge when it falls through a potential of one volt, equivalent to 1.602×10^{-19} J. The more useful unit is the mega (million) electron volt, MeV.

McMillan, Kamen and Ruben assigned the original identification of the 60 day activity to Fomin and Houtermans in 1936 (17), but these two appeared not to have produced this activity but simply mentioned its discovery by Amaldi and Fermi. However Fomin and Houtermans became credited with the first observation and this confusion was not resolved until 1951 (18). None of the other activities reported prior to 1938 have proved to be correct.

As with platinum, the most prolific decade for the discovery of iridium isotopes was the 1960s with Antti Siivola, who was then at the Lawrence Radiation Laboratory, Berkeley, California, producing and identifying seven new isotopes in 1966 (19). More recently there has been a concentration on the proton-rich isotopes, and in 1995 a British-American team, one of the leading members of which was Philip J. Woods, announced the production of the three proton-emitting isotopes ^{165}Ir , ^{166}Ir and ^{167}Ir and this research group was therefore the first to cross the proton drip line in iridium (20, 21). More recently two groups have independently discovered the even lighter proton-emitting isotope ^{164}Ir , the first at the Department of Physics, University of Jyväskylä, Finland (22), and the second by the British-American team mentioned above (23). The discovery of four particle-unstable isotopes (i.e. proton emitters) for one element is a record. Because the half-life of ^{164}Ir is likely to be less than 100 μs it is likely that there may be extreme difficulty in producing and identifying even lighter isotopes.

In the Table of the Discoverers of the Iridium Isotopes the date of discovery is a manuscript or conference date, or, if unavailable, then a publishing date. The half-lives are mainly those selected in the NUBASE database (24) with new or revised values being referenced in the Notes to the Table.

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The Author

John W. Arblaster is Chief Chemist working in metallurgical analysis at Coleshill Laboratories. He is interested in the history of science and in the evaluation of the thermodynamic and crystallographic properties of the elements.

The Discoverers of the Platinum Isotopes

In the earlier review on platinum isotopes (1), on page 174, the β^- decay mode of ^{202}Pt was inadvertently omitted.

On page 177, the second and third lines on the left hand column should be: "Table of Isotopes" and the fourth line should read "In the Table of the Discoverers of the Platinum Isotopes, the mass number of each isotope..."

Recyclable Microencapsulated Osmium Tetroxide Catalyst

Osmium tetroxide, OsO_4 , is an efficient oxidation catalyst, well known for olefin hydroxylation and dihydroxylation reactions. For the catalytic asymmetric dihydroxylation (AD) of olefins, addition of a chiral ligand, such as $(\text{DHQD})_2\text{PHAL}$, to the OsO_4 reaction mixture, gives access to a wide range of enantiomerically pure vicinal diols. The chiral ligand is based on a bisquinoline alkaloid with a phthalazine core (1).

However, OsO_4 is highly toxic and volatile and difficult to use, and to avoid hazards OsO_4 has sometimes been bound to polymers. Replacing organic solvents by water for chemical reactions is an additional interest.

Now, a team from The University of Tokyo, Japan, have developed a microencapsulated OsO_4 system, based on poly(phenoxyethoxymethylstyrene-*co*-styrene) (PEM-MC OsO_4) (2) which can perform AD of olefins with water as the sole solvent without catalyst leaching. The system uses a H_2O -acetone solvent and $\text{K}_3\text{Fe}(\text{CN})_6$

cooxidant, with $(\text{DHQD})_2\text{PHAL}$ ligand added to PEM-MC OsO_4 catalyst; acetone is then removed. Addition of a non-ionic surfactant, Triton[®] X-405 (octylphenoxy-polyethoxyethanol) was found to increase yield and ee and reduce Os leaching. Issues around catalyst solubility were resolved by adding the ligand directly to the reaction mixture. Product diols were obtained in better yield without catalyst deactivation even after three runs. Os leaching was completely suppressed by neutralising with aqueous H_2SO_4 . Other olefins behave similarly and the PEM-MC OsO_4 can be separated by filtration, recovered and reused without loss of activity.

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