特別講演

第1日　9月26日（月）

特別講演1　　J. V. KRATZ

第2日　9月27日（火）

特別講演2　　P. P. POVINEC

特別講演3　　森永　晴彦

1S01

CHEMICAL PROPERTIES OF THE TRANSACTINIDES

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After the pioneering studies of some basic chemical properties of the early transactinide elements 104 and 105 in the 1970's that confirmed the placement of these elements in group 4 and 5 of the periodic system there is renewed interest in studying in more detail the chemical properties of the transactinides. This is because computer–controlled automated systems have greatly enhanced our ability to rapidly and reproducibly perform the hundreds and sometimes thousands of successive separations required to obtain statistically significant results, and because relativistic quantum–chemical codes are now becoming capable of modelling heavy complex molecules. By comparison of the chemical behaviour of elements 104 and 105 with that of their lighter homologs Zr and Hf, and Nb and Ta, respectively, and with some pseudo–homologs in the light actinides, and by comparison of the details observed experimentally with results of relativistic MO–calculations it is hoped to evaluate the role of relativistic effects in the chemistry of these very heavy elements.

In this paper, a review is given of the production, transport, and detection of the isotopes 78–s $^{261}104$ and 34–s $^{262}105$ with which the chemical studies are performed. These isotopes are produced an atom–at–a–time, and the validity of single–atom chemistry is discussed. Next, the chemical techniques are presented: These include on–line isothermal gas chromatography of chlorides and bromides, and aqueous–phase chemistry studies using liquid–liquid extraction and anion– or cation–exchange chromatography. The equipment used in these separations named OLGA, HEVI, ARCA, and SISAK, is introduced.

The gas–phase studies for the group–4 chlorides have established the following series in volatility: Zr > 104 > Hf. The results on the group–5 bromides establish the series Nb > Ta > 105. Results on the volatility of 105 chlorides are still preliminary but indicate a higher volatility than for the 105 bromides.

In aqueous solutions, at high Cl^- concentrations, TBP extractions of element 104 indicate that, unlike Zr^{4+}, Hf^{4+}, and Th^{4+}, 104^{4+} forms anionic chloride species (which do not extract), similar to those of Pu^{4+} at higher Cl^- concentrations. Also element 105, in extractions with triisooctyl amine(TiOA) from HCl solutions, shows a rather unexpected behavior. At all HCl concentrations, 105 is found to behave similarly to Nb and Pa, and to be very different from its closest homolog, Ta. Nb is known to form complexes of the $[NbOCl_4]^-$ type which is also known for Pa. These are in hydrolysis equilibrium with $[Pa(OH)_2Cl_4]^-$. For Ta, stronger, largely covalent complexes of the pure halide type such as $[TaCl_6]^-$ are predominant. We have concluded that the complex structures of element 105 must be of the Nb, Pa type. Pershina et al., by using the Dirac–Slater Discrete Variational Method(DS–DVM), performed calculations on the pure halides $[MCl_6]^-$ and on $[MOCl_4]^-$ and $[MOCl_5]^{2-}$, respectively, with M = Nb, Ta, Pa, and 105. They find that, for the pure halide complexes, the Ta complex shows by far the highest overlap population (a measure for the covalent bonding strength). According to the overlap populations, Nb and Pa have the tendency to form the oxygen containing structures with the strongest tendency to form the oxyhalide complexes for element 105. It is gratifying to see that this analysis gives results that are consistent with the experimental observations. This gives hope that further comparisons of this type will increase our understanding of the sometimes surprising chemical properties of the transactinide elements. Preparations are under way to study for the first time the chemical properties of element 106 both in the gas phase and in aqueous solutions.

2S01

RECENT DEVELOPMENTS IN LOW-LEVEL RADIONUCLIDE ANALYSIS OF MARINE SAMPLES

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Recent developments in radiometric and mass spectrometry techniques for low-level radionuclide analysis are reviewed.

The main requirements for low-level radionuclide analysis of marine samples are discussed and operational characteristics of alpha (Si), beta (LSS) and gamma (Ge) spectrometers are described. New developments in **underwater** gamma spectrometry are highlighted.

Considerable improvements in the parameters of ultra low-level counting systems can be obtained by operating low background detectors in an **underground environment**. A background reduction of more than an order of magnitude is possible when operating detectors at depths of a few 10 m w.e. The underground installations would enable to measure radioactivity levels down to a few μBq. There is simple advice for further development in low-level counting : use of construction materials with low intrinsic radioactivity and **go underground**.

Recent developments in the **mass spectrometry** sector (AMS, ICPMS) are briefly discussed as well.

2S02

^{42}Ar－^{42}Kゼネレータについて

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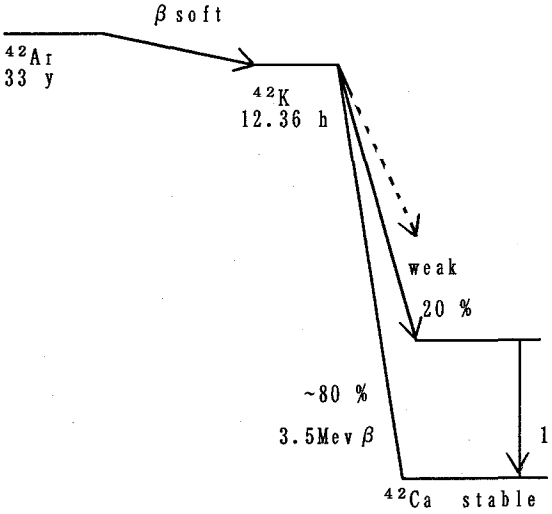
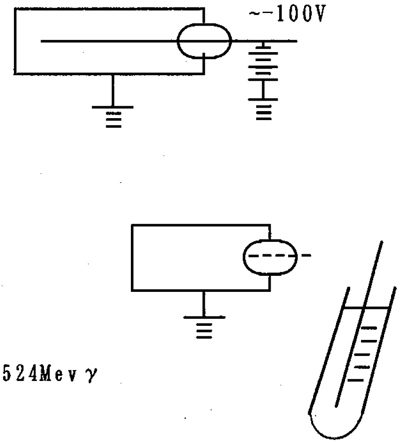
約10年程前から、ミュンヘン工科大学のコンパクトサイクロトロンの7Mevのトリトンビームを用いて^{42}Arの生産が行われ、既に40μCi近くの^{42}Arが日本にも送られ、いろいろな分野で用いられている。^{42}Arの崩壊型式は図(1)に示す。



図(1) ^{42}Arの崩壊型式



図(2) ^{42}Ar-^{42}Kゼネレータ

また図(2)には^{42}Ar－^{42}Kゼネレータを示す。^{42}Arと平衡にある^{42}Kは～-100ボルトの電圧でワイア上に集められ、これは引きぬいて水にとかして、無担体の^{42}Kをいつでも取り出される。1989年より4年間毎年アイソトープ協会で、この、ゼネレータの使用経験と展望と題する一日のワークショップが行われた。今回はこの生産、供給の意義、利点欠点、生産の現状、使用経験、なさるべき仕事等について報告する。

ON THE ^{42}Ar-^{42}K GENERATOR

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33 years ^{42}Ar decays to ^{42}K which further decays with β and γ to stable ^{42}Ca. ^{42}K can be milked very conveniently by appling ~-100 Volts on a wire inserted in the ^{42}Ar container. A carrier-free ^{42}K solution can be obtained very conveniently. The ^{42}Ar activity has been produced in the cyclotron laboratroy of the Technical University of Munich and has been used more than 10 years in different branches in Japan. In this lecture experiences obtained therewith those uses will be presented and its merit and demerit will be discussed.