# RECENT PROGRESS IN ILLINIUM.

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The discovery of the element illinium, or element 61, by the American chemists, Harris, Hopkins and Yntema early in 1926, brings the list of elements discovered within the past five years to four, and brings the list of elements presumed to exist more nearly to completion. At the time Moseley discovered the relation between the frequency of any line in the X-ray spectrum of any element and its atomic number there were seven gaps in the list of the elements. The missing members of the atomic series as listed at that time were elements 43 and 75, analogues of manganese, 61, a rare earth element, 85 a halogen, 87 an alkali metal, and an element 91. Moseley assumed that celtium, a member of the rare earth group, for which Urbain claims the discovery, filled the space assigned to element 72. The present view seems to be that element 72 should be called hafnium, as discovered by Coster and Hevesy in 1923. It is not considered as a rare earth but as a homologue of titanium and zirconium. Number 91, a radioactive product of the actinium series was named protoactinium by Soddy, Hahn and Meitner in 1918. Mendeleeff's eka-manganese and dvi-manganese were announced by Noddack and Tacke and named masurium and rhenium respectively. Druce and Loring also claim priority for these latter two elements.

The most recently discovered element is the one of atomic number 61, and has been named illinium after the state and university in which the research leading to its identification was carried out. The announcement of its detection was first made in March, 1926 by Harris, Hopkins and Yntema at the chemical laboratory of the University of Illinois. Its discovery is of special interest inasmuch as the group of elements occurring between lanthanum 57 and lutecium 71, commonly called the rare earths, is now known to be complete. The rare earth group has always given difficulty when an attempt has been made to place it in the periodic table, there being no indication of the possible number of elements included in the group. Their complete chemical separation is also a matter of great difficulty. Moseley's relation between the various chemical elements was of extreme importance in defining the number of elements to be expected in this group and in stating that the missing element should occupy a position between neodymium 60 and samarium 62. This latter fact has been a guiding factor in the research carried out by the numerous investigators working with the idea of isolating element 61.

There were several lines of evidence offered as the basis for the discovery of illinium, and it may be of interest to review these very briefly. One of the problems in which the Bureau of Standards was interested was the mapping of the red and infrared regions of the spectra of all known elements, and material was furnished by the University of Illinois for this work. In the published reports on neodymium and samarium, Kiess gives about 1500 lines for each of these elements, and in addition gives the wave lengths of some 130 lines which are common to both spectra. These lines could not be identified with the spectra of any other known element, and it was suggested that these lines might be due to a new element. Concentration and isolation of the element causing these lines was then begun. Yntema carried out an X-ray analysis of the intermediate fractions of some neodymium-samarium fractions which had been through a considerable number of fractionations but the results were negative. He observed, however, five lines common to both elements in a small region of the ultra violet, while studying the arc spectra of these elements.

A better method of concentration seemed to be needed and a study of the various salts used for the fractionation of the rare earths was made. The double magnesium nitrates have solubilities which increase with increase of atomic number, and element 61 would be expected to concentrate between neodymium and samarium. James at New Hampshire has shown that when the bromates are used for fractional crystallization, the solubilities of the rare earths first show a decrease in solubility with increase of atomic number, reaching a minimum with europium and then an increase in solubility with increase of atomic number. As a result the order of crystallization is europium as the least soluble member of the series, gadolinium, samarium, illinium, terbium and neodymium. If only the neodymium-samarium rich fractions of a series of double magnesium nitrates are converted into rare earth bromates, the order of solubility is for practical purposes reversed. Harris carried out an extensive fractionation of the neodymium and samarium rich material in this way. While so doing, he observed that the absorption bands in the visible region characteristic of neodymium and samarium began to disappear in the intermediate fractions, and that at the same time a very faint line of wave length 5816Å units began to appear. Later another line at 5123Å units was observed to grow stronger in the intermediate fractions. Naturally the question arose as to whether these new lines belonged to a new element and on further study, it was decided that these lines were due to illinium.

An X-ray analysis of the material used by Harris in his work was carried out at the University of Illinois. Five determinations of the $L\alpha_1$ were obtained the values agreeing very well with the calculated value. A single determination for the $Lb_2$ was obtained and there was a faint indication of the $Lb_2$ on one plate but it was not accepted. The question always arises when an X-ray analysis of this type is carried out as to whether there are any first, second or third order lines of other elements which might conflict with those of the element in question. After careful consideration of the experimental work, it was decided that there was no conflict between the lines of these other elements and those of illinium.

That the research at the University of Illinois was not the only work being carried forward with the idea of isolating element 61 may be seen in that almost immediately after the initial announcement of the discovery by the American chemists, several papers appeared from other laboratories. Meyer, Schumacher and Kotowski were among the first to publish the results of their work upon illinium. They used the bromate and double magnesium nitrate method of separation, and were able to secure the K series lines of the new element.

Further confirmation of the discovery of illinium has been made by the admirable work of Rolla and Fernandez at the University of Florence. Working on a small amount of didymium material, which was fractionated as the double thallium sulphate, they obtained evidence for the existence of the new element by the X-ray absorption method of the K series. A description of this work, instead of being published at the time, was placed in a sealed package in the vaults of the Academy of Lincei in 1924, and the study of a larger supply of the material was begun. In the meantime the discovery was announced by the American chemists. Following this, Rolla brought forth his "Plico Suggellato" from the vaults of the Academy. Upon the basis of the information contained in this sealed packet, he claims priority for the discovery of the element and insists that it be called "florentium." His first announcement came some three months after the initial declaration of the discovery by the American chemists, Harris, Hopkins and Yntema. At the present time there is considerable of a controversy taking place in the literature as to whether the Americans or the Italians discovered illinium.

In our own country, James and Fogg at New Hampshire showed the presence of element 61 in their material. Some samples carefully prepared from the intermediate neodymium-samarium fractions secured from gadolinite, xenotime and monazite were examined by Cork at Michigan. The publication of these lines is convincing evidence of the identification of element 61.

On the other hand, there are investigators who doubt the existence of element 61, and discredit the announcements made. Professor Wilhelm Prandtl, of Munich, in reviewing the evidence given seems unwilling to be convinced. He severely criticizes the work of Harris, Hopkins and Yntema. He seems unable to attach any importance to the new absorption bands, considers the strange lines in the arc spectra as insignificant, and criticizes the X-ray analysis because a vacuum spectrograph was not used. He criticizes the work of Rolla and Fernandez in the same way, and claims that Meyer, Schumacher and Kotowski used too much of mixture, hence getting lines which could be attributed to element 61. Professor Prandtl himself has made a very careful search for several years for element 61, but all of his results were negative. He criticizes the work done upon masurium and rhenium in the same way. Auer von Welsbach claims that element 61 does not exist quoting Prandtl's work and his own.

Dr. W. A. Noyes and G. V. Hevesy have reviewed the evidence submitted and both give credit for the discovery to the American chemists Harris, Hopkins and Yntema. In the English books appearing within the past year, the element is mentioned as illinium.

Since the initial announcement of the discovery, the work of isolation of the element has been continued on a much larger scale. This research is being carried along in a number of different ways. A large quantity of monazite residues have been fractionated using the double magnesium nitrates and the bromates as the means of separation of the rare earths. Other methods of fractional crystallization, such as the perchlorates, simple nitrates, double manganese nitrates, etc. are being used.

The separation of the rare earth elements by means of fractional precipitation methods and the determination of the relative basicity of illinium is also being studied, using ammonium hydroxide and sodium nitrite as the precipitants. The separation of illinium from its neighbors by the Kendall ionic migration method, a method depending upon the variation of ionic velocity is also being tried. Considerable work is also being carried out on other ores as potential sources of illinium. Cerite, American samarskite, allanite, gadolinite, tscheffkinite, are among the ores that are being studied at the present time. There is a supply of several other rare earth ores on hand, all of which will be put through the process as soon as possible. Some research is also being carried out on a method of separation of illinium which makes use of the difference of the magnetic susceptibilities of the rare earths. The most promising methods for the separation of illinium seem to be the bromate and double magnesium nitrate methods of fractional crystallization. The determination of the relative basicity of illinium is very tedious work, although the evidence so far seems to indicate that illinium will fall between neodymium and samarium in basicity.

In addition to the actual work on the separation of the element, a study is being made of the absorption spectra of these elements in order to determine the exact conditions by means of which the absorption spectra can be depended upon as a positive means for following the process of fractionation. The X-ray apparatus for the emission spectra work has been reconstructed, and a Siegbahn vacuum spectrograph has been obtained for this work. The analysis of the various materials being used is under way at the present time.

This is, in a very brief form, the status of illinium at the present time, but the research under way at the time being should bring out much information concerning the new element within the next year or two.

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