

# Determination of Rhenium in Molybdenum and Tungsten by Neutron Activation

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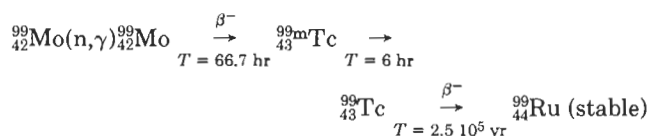
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Rhenium is an impurity which often occurs in molybdenum ores (1–4). It may also occur in pure molybdenum, because it seems that rhenium cannot be completely eliminated by the purification process used in our laboratory (5).

In the case of tungsten, concentrations of about 10  $\mu\text{g/g}$  in the pure metal were reported (6). In our laboratory, preliminary results obtained by spark source mass spectrometry showed concentrations varying from 2 to 40  $\mu\text{g/g}$  in pure industrial tungsten.

As far as we know, in the literature, rhenium has been determined mostly in rocks or compounds containing large quantities of molybdenum or tungsten (6–11). To reach a limit of detection better than  $10^{-9}$  g, we chose thermal neutron activation analysis. The nuclear reaction we use is  $^{187}_{75}\text{Re}(n,\gamma)^{188}_{75}\text{Re}$ . This reaction has a cross section of 72 barns with an isotope whose natural abundance is 62.93%. The half life of  $^{188}\text{Re}$  is 16.8 hr and the most intensive  $\gamma$  radiation is 155 keV. It would be also possible to use the  $^{185}\text{Re}(n,\gamma)^{186}\text{Re}$  reaction, which has a similar cross section by abundance product. But  $^{186}\text{Re}$  has a half life of 90 hr which needs a longer irradiation and produces more radioactivity from the isotopes of the matrix.

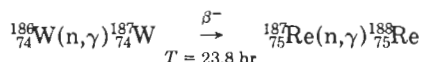
In the case of molybdenum, the most radioactive isotopes produced from the matrix are  $^{99}_{42}\text{Mo}$  and  $^{99\text{m}}_{43}\text{Tc}$ . They are created according to the following scheme:



Molybdenum and technetium must be separated before measuring the radioactivity of  $^{188}_{75}\text{Re}$ . Technetium and rhenium have very similar chemical properties and technetium must be separated during or after the separation of molybdenum to avoid further production by radioactive decay.

In the case of tungsten, the irradiation leads mainly to  $^{187}_{74}\text{W}$ , whose half-life is 23.8 hr. The radioactivity of this isotope is so intensive that tungsten must be separated in a hot cell with remote handling equipment.

Tungsten may lead to an interference according to the following scheme:



The calculations show that the apparent concentration of rhenium is less than  $0.3 \cdot 10^{-3}$   $\mu\text{g}$  per g of tungsten after 25 min. of irradiation in a thermal neutron flux of  $5 \times 10^{12}$   $\text{cm}^{-2} \text{sec}^{-1}$  (12).

**Principle of Chemical Separations.** Many methods of separating rhenium have been published. One of these methods, widely used, is the extraction of the perrhenate of tetraphenylarsonium (13). This method is selective for Re and Tc, but the reextraction appeared to be rather difficult. Some other methods of extraction have also been published (11, 12, 14–17).

Numerous separations using organic or inorganic exchangers have been reported (18–25). These methods are difficult to apply in order to separate a very radioactive matrix.

We used the possibility of extraction of rhenium in a ketone from a basic aqueous solution (26). Experiments showed that rhenium(VII) (in a concentration of 3 mg/l.) is extracted by acetone with a yield better than 98% from an aqueous solution containing NaOH in a concentration from 2 to 7M. The percentages of molybdenum and tungsten extracted in the organic phase from a 7M NaOH solution are 0.3 and 0.2%, respectively.

Technetium produced from molybdenum is extracted together with rhenium. The pertechnetates being more reducible than the perrhenates, we studied the possibility of keeping technetium in the aqueous phase after a selective reduction, for instance by hydroxylamine sulfate. These experiments did not lead to good results, as technetium was always partially extracted and as molybdenum was reduced and precipitated. For these reasons, in the case of the analysis of molybdenum, we used another step for the separation of rhenium from technetium. This separation was achieved by using an anion exchange resin in a medium containing HCl and  $\text{NH}_4\text{SCN}$  (27–29).

The rhenium(VII) oxide being volatile, we checked that there would be no loss of rhenium during the evaporation in the determination procedure.

## EXPERIMENTAL

**Irradiation.** The samples of Mo or W (from 0.1 to 1 g) are irradiated for 20 min. in a thermal neutron flux of  $3$  to  $4 \times 10^{12}$   $\text{cm}^{-2} \text{sec}^{-1}$ . At the same time, we irradiated standards obtained by depositing 10  $\mu\text{l}$  of a titrated solution on filter paper (Ederol 4 M). This solution was obtained by dissolving a known quantity of 99.95 rhenium (Koch-Light) in aqua regia. Each standard contains between 1 and 2  $\mu\text{g}$  of Re.

**Treatment after Irradiation.** Standards are dissolved in a  $\text{HNO}_3$  solution and adjusted to 10  $\text{cm}^3$ . Molybdenum is pickled in a solution containing: concentrated  $\text{H}_2\text{SO}_4$ , 46%; concentrated  $\text{HNO}_3$ , 8%; water, 46%. Tungsten is pickled in a solution containing 10M HF, 50%; 12M  $\text{HNO}_3$ , 50%.

**Chemical Procedure for Molybdenum.** Molybdenum is dissolved in 40  $\text{cm}^3$  of aqua regia, containing 100  $\mu\text{g}$  of Re carrier. Just after dissolution, the solution is evaporated to 10  $\text{cm}^3$ , adjusted to approximately 7M NaOH in a volume of 30  $\text{cm}^3$  and shaken for 2 min. with two volumes of 30  $\text{cm}^3$  of acetone freshly equilibrated with 7M NaOH. The organic phases are washed with equal volumes of 7M NaOH, mixed together, and evaporated after addition of dilute HCl. All the above operations must follow each other without interruption, otherwise a decrease in the extraction yield may be observed. The concentration is then adjusted to 0.2M HCl in a volume of 20  $\text{cm}^3$ . This solution is poured at a flow-rate of 0.2  $\text{cm}^3 \text{min}^{-1}$  on a column of exchange resin Dowex 1 X-10 (Cl<sup>-</sup> form, grain size: 56–125  $\mu\text{m}$ , height: 120 mm, diameter: 6 mm). The resin is washed by 30  $\text{cm}^3$  of 0.2M HCl and rhenium is then eluted by 60  $\text{cm}^3$  of 0.1M HCl containing 5%  $\text{NH}_4\text{SCN}$ . Technetium is kept in the resin. The solution containing rhenium is evaporated to 10  $\text{cm}^3$ .

**Chemical Procedure for Tungsten.** The sample is dissolved in a polytetrafluoroethylene vessel by a solution containing 10  $\text{cm}^3$  of concentrated HF, 5  $\text{cm}^3$  of fuming  $\text{HNO}_3$ , and 100  $\mu\text{g}$  of Re carrier. The solution is then evaporated and HCl is added until HF is com-

**Table I. Efficiency of the Chemical Separation**

Metal analyzed	Yield for Re, %	Remaining matrix, %
Mo	99	$< 10^{-2}$
W	95 ± 2	$10^{-3}$

**Table II. Determination of Re in Various Mo Samples**

Mo sample	Concentration Re, $\mu\text{g/g}$
Ugine Kuhlmann	0.014
Cime Bocuze	0.029
Metallwerk Plansee	0.082
Climax	0.93
Ammonium paramolybdate, Ugine Kuhlmann	0.0037
Reduction of paramolybdate	0.0017
Paramolybdate purified by ion exchange and then reduced	0.0069

pletely removed. The solution is then made approximately 7M NaOH by addition of 10M NaOH (if HF was not completely removed, we observed precipitation at this stage). The volume is about 30 cm<sup>3</sup>. Rhenium is extracted by an equal volume of acetone freshly equilibrated with 7M NaOH. The organic phase can now be handled out of the hot cell. The acetone is evaporated and aqua regia containing 1 to 2 mg of inactive tungsten is added. The solution is evaporated and adjusted to 7M NaOH in a volume of 30 cm<sup>3</sup>. Rhenium is extracted twice by 30 cm<sup>3</sup> of acetone. The organic phases are washed by 6M NaOH, put together, and evaporated to 10 cm<sup>3</sup> for radioactivity measurements.

**Radioactivity Measurements.** Measurements are performed on the 155-keV  $\gamma$ -ray using a Ge-Li detector coupled to a pulse height analyzer. Standards and samples are all in solution. The results of countings are computed according to a program described earlier (30). The half-life of <sup>188</sup>Re is generally checked.

**Spark Source Mass Spectrometry.** We used a double-focusing Mattauch-Herzog mass spectrometer manufactured by Thomson-C.S.F. The source and the electrostatic and magnetic analyzers are each pumped by sputtering titanium in a Vaclon pump. The mass spectrum is recorded on a 15-inch  $\times$  2-inch Ilford Q2 photo plate and concentration determined by optical density measurements of peaks corresponding to masses 180, 185, and 187.

## RESULTS AND DISCUSSION

Before applying the method to actual samples, we measured the yield for rhenium in the whole scheme of separations by adding radioactive Re during the dissolution of inactive Mo or W. We also measured the percentage of radioactive Mo and W remaining in the last fraction after the separations. These results are shown in Table I. In the case of W, the yield is lower than in the case of Mo. This difference is explained by the greater difficulty in performing separations in a hot cell.

In the case of molybdenum, the efficiency of the separation depends also on the remaining radioactivity of technetium. The main factor is the flow rate on the ion exchange column, which must not exceed 0.2 cm<sup>3</sup> min.<sup>-1</sup>.

With the above conditions of irradiation, a counting time of 3 hr on a Ge-Li detector of 50-cm<sup>3</sup> capacity and 2.25-keV resolution for 1.33 MeV, the limits of detection for Re are  $1.5 \times 10^{-9}$  g in Mo and  $0.2 \times 10^{-9}$  g in W. These figures are calculated according to L. A. Currie (31). The limit of detection is higher in Mo because of the presence of traces of technetium.

The precision was measured from the reproducibility of determinations in molybdenum and tungsten. It depends mainly on the counting statistics. In the case of molybdenum, it is about  $\pm 5\%$ . For the determinations in tungsten,

**Table III. Determination of Re in Various W Samples, g/g**

Sample number	Mass spectrometry	Activation analysis
1	$6 \times 10^{-6}$	$1.4 \times 10^{-9}$
2	$1.3 \times 10^{-6}$	$0.89 \times 10^{-9}$
3	$45 \times 10^{-6}$	$0.24 \times 10^{-9}$
4	$4.3 \times 10^{-2}$	$4.5 \times 10^{-2}$
5	$19.8 \times 10^{-2}$	$23.4 \times 10^{-2}$

it reached  $\pm 20\%$  because of the very low concentrations, not far from the detection limit.

If very accurate results are needed, a correction for thermal neutron self shielding must be done. This effect depends on sample weight and geometry and on neutron thermalization. The correction may be as much as 10–20% in tungsten matrices (10% for 0.1-g samples, 20% for 1-g samples). For molybdenum matrices, the effect of neutron self shielding is much less, resulting in Re values low by 2–4% (for 0.1-g and 1-g samples, respectively).

Table II shows results of determination of Re in various molybdenum samples. The concentration of Re depends much on the source of molybdenum but does not exceed 1  $\mu\text{g/g}$ . The paramolybdate used for the preparation of high-purity molybdenum contains only some  $10^{-9}$  g/g of Re. The determination also shows that the purification process used in our laboratory does not reduce the concentration of Re. If the source of molybdenum were not well chosen, rhenium would have been the major metallic impurity of the purified metal, as the concentrations of the other impurities of this type are all less than 1  $\mu\text{g/g}$  (5, 32).

Table III shows the results of the determinations of Re in tungsten, performed by activation analysis and spark source mass spectrometry. A great discrepancy is observed between the two methods.

To check the results, we have doped one of the pure tungsten samples with rhenium. The doping was achieved by irradiating tungsten in neutrons and waiting for the complete decay of <sup>187</sup>W to <sup>187</sup>Re. The calculated concentration of rhenium (mainly <sup>187</sup>Re) was 2.1  $\mu\text{g/g}$ . A determination by activation analysis according to the described procedure gave 2.3  $\mu\text{g/g}$ . This result confirms the accuracy of the activation method. The small discrepancy of 0.2  $\mu\text{g/g}$  may be due to a bad knowledge of the cross section and of the epithermal neutron flux for the calculation of the predicted value.

The same doped sample was submitted to spark source mass spectrometry. The peaks corresponding to masses 185 and 187 were approximately of an equal amplitude, which is in discrepancy with the abundances of the two isotopes of Re (especially with the enrichment in <sup>187</sup>Re). These equal amplitudes may be explained by the formation of <sup>184</sup>WH and <sup>186</sup>WH ions, as the abundances of <sup>184</sup>W and <sup>186</sup>W are practically equal (respectively, 30.46 and 28.41%). At the present time, we cannot say whether hydrogen comes from the sample or from the residual gas.

## CONCLUSION

The activation methods for rhenium determination we describe here are very sensitive. The limit of detection of  $10^{-9}$  g may be improved, if needed, by increasing the time and flux of irradiation. This limit is achieved because of the nuclear properties of rhenium and the efficiency of the chemical separations. This efficiency is mainly due to the extraction method of rhenium by a ketone from a basic medium. It would be worthwhile to use extractions from basic media more frequently than nowadays.

The determinations we performed brought interesting metallurgic and analytical results. We showed that rhenium at the ppm level may be the major metallic impurity in the pure molybdenum, if the source of metal is badly chosen. In tungsten, the concentration of rhenium is very low, in discrepancy with earlier results. In this case, we discovered that spark source mass spectrometry has a blank of some  $\mu\text{g}$  of rhenium per g of tungsten, when the actual concentration measured by activation analysis was of some  $10^{-9}$  g/g. On the contrary, the agreement between activation analysis and mass spectrometry is good for alloys containing some percent of rhenium.

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