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## Modified Jones reductor for reduction of $\text{Eu}^{3+}$ TO $\text{Eu}^{2+}$ in solution

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### ABSTRACT

The possibility of a modified Jones reductor that can be used to reduce Europium (Eu) for the purpose of doping in thermally unstable host lattice in solution was investigated. A modified Jones reductor which can be used to reduce  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  and doping same into thermally unstable host lattice was constructed. It was then used to reduce Europium in solution. The reduced Europium was analysed by measuring its emission using Fluorolig-3 spectrofluorometer. The constructed Jones reductor consisted of a column (13cm x 2.5cm), a receiver with a neck of about 2.5cm, an adaptor of diameter NS14.5cm and three taps of 2.5cm each for the exits. A solution of prepared Europium salt was passed through the modified Jones reductor to reduce  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$ . The result showed that within the limit of error almost 99% reduction was achieved. In conclusion, the modified Jones reductor can be used to reduced Europium and dope it into compounds that are difficult to dope through the melt method.

**Key words:** europium, modified jones reductor, reduction.

### INTRODUCTION

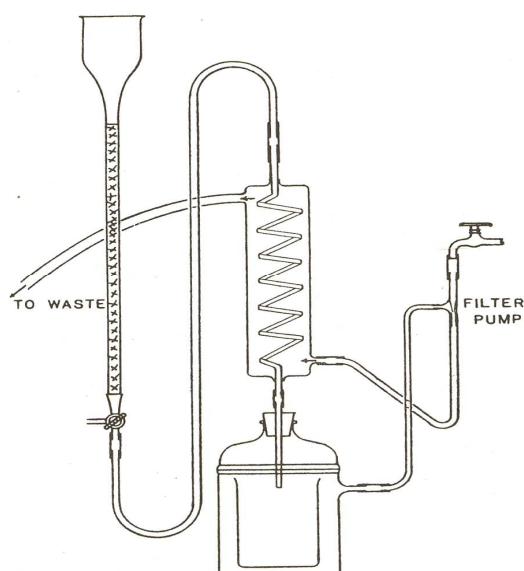
Some few methods are available in the literature for the reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$ , some examples of these methods are as follows: Selin. D.L et al [1] applied  $\gamma$ -irradiation to reduced Eu (III) to Eu (II) in aqueous solution of a mixture of rare earth elements. Selin. D.L et al [2] in another publication used a method of radiolytic reduction in dilute aqueous solution. They observed that the reduction of Eu (III) was enhanced by the presence of  $\text{Sm}^{3+}$ . Electrolytic reduction of Eu (III) in acidic chloride solutions with titanium cathode was used by Hirato et al [3] to examine the feasibility of the rare earth separation. They claimed to achieved complete reduction of 0.1mol of  $\text{EuCl}_3(\text{aq})$  solution. But they observed that the final percent Eu(III) reduction of the solution from an industrial europium purification process which contained other rare earths, was lower than that of a synthetic  $\text{EuCl}_3$  single electrolyte solution.

Polarographic reduction of europium ions on mercury-drop electrode in the presence of halide ions was used by Levitskaya et al [4] to determine the amounts of europium in Eu-base alloys. In 1987 Kaneko et al [5] used a method similar to what is being used in this work i.e reduction of europium using zinc fixed beds to separate europium from other rare earth metals. They passed their solution in the fixed bed for five hours at 2.4L/h rate and obtained 97% reduction. Other methods obtained in the literature that can be mentioned here include, one-electron reduction induced by the irradiation of gamma-ray or UV light, Isida et al [6], electrochemical reduction by Nemeč et al [7], chemical reduction in hydrochloric acid by Atanasyants et al [8] and reduction on rotating disk platinum and copper electrodes by Louka et al [9].

A Jones Reductor is a convenient apparatus for effecting the reduction of certain compounds. It consists of a column of amalgamated zinc contained in a long glass tube, provided with a stop cock through which the reduced solution

may be drawn. The Jones reductor give an advantage that a large surface is exposed to the substance to be reduced, as such a zinc column is much more efficient than pieces of zinc placed in the solution. The basic Jones reductor is not suitable for some processes; example is reduction of the lanthanides which are easily oxidised back to their trivalent state. For this reason many people have tried to modify the Jones reductor to be used for different purposes, such as in this work. Some examples of work done in the literature on modified Jones Reductor include the following:

- Taeble in 1939 [10] observed that the efficiency of a traditional Jones reductor is governed by the rate at which the solution containing the substance to be reduced flows through the reductor. The ordinary Jones reductor has no means of regulating or controlling rate of flow, so it is difficult to maintain a particular rate throughout the reduction. This led him to investigate into modification of the reductor. (His work titled “modified Jones reductor” was then published. According to his result, the modified Jones reductor enables one to obtain a definite and constant rate of flow. This he did by fitting the delivery tube of the reductor with replaceable grounduated glass capillary tubes of various sized orifices.
- Another modified Jones reductor was invented by Edwards [11] and is shown here in fig1 below. The exit tube of the Jones reductor is fitted with a three-way tap, one tube opening to the air and the other being connected by means of a vertical glass tube to the top of a cooling coil surrounded by cooling water. The lower end of the coil is connected to a witts filter apparatus, in order to collect the solution in a beaker. This modification was particularly used for solution that is best reduced when warm or hot.



**Fig 1: Modified Jones Reductor [11]**

- In 1984 Azad and co [12] used the Jones reductor for a metal speciation. They passed the solution through a mini-column incorporated in a flow injection system for spectrophotometric determination of iron (III) and simultaneous determination of iron (II) and total iron. They concluded that reduction of iron (III) to iron (II) was achieved efficiently in a small Jones reductor column, with little effect on sample dispersion.
- In 1987 Kamil *et al* [13] also used the flow-injection method to determine europium after on-line reduction. They claimed that the reductor offers a very selective method for the determination of europium (III) in the presence of all lanthanides, because samarium, ytterbium or any other lanthanides are not reduced. Their conclusion was that, the incorporation of a reductor minicolumn into a flow-injection system provides simple and highly selective procedures for the determination of europium (III). Their flow system shown provides a rapid and reproducible method of producing europium (II) without the need for the elaborate precautions to prevent its re-oxidation.

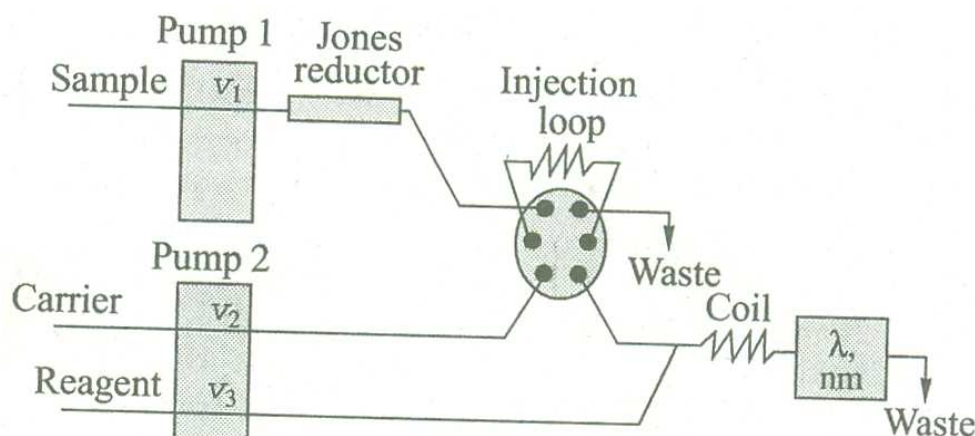


Fig 2: Scheme of a flow injection system [14].

Where  $V_1$  = Rate of pumping europium (III) into the Jones reductor.

$V_2$  = Rate of injection into the carrier flow.

$V_3$  = Rate of flow of the redox reagent.

• In 2001 a similar work was done by Shpigun *et al* [14], Fig.2 above shows their flow-injection diagram. They observed that the reduction of europium (III) in a Jones reductor opens up a possibility of developing selective method for the determination of this metal in the presence of all other rare-earth elements. Their system made it possible to avoid the problem of handling europium (II) after reduction, because reduction and determination are performed in closed flow-injection system. This implies detecting this unstable oxidation state within less than 30seconds after it formation in solution. Their investigations showed that the conversion degree of europium (III) to europium (II) depend on the sample acidity and the flow rate. The flow rate of 0.4 to 0.6ml/min was optimum. When they used metal solutions prepared in 0.1M HCl, the degree of reduction was 75%, but in 0.25m HCl the degree of reduction was up to 95%. From their results therefore, it can be seen that although they used a closed system, they did not obtain 100% reduction.

## MATERIALS AND METHODS

### Construction of the Modified Jones Reductor:

The Jones reductor was designed in the University of Siegen Inorganic Chemistry laboratory.

The constructed Jones reductor consisted of a column (40cm x 2cm), a receiver with a neck of about 2.5cm, an adaptor of NS14.5cm and three taps of 2.5cm each for the exits. The exact specifications of the Jones Reductor are shown in table 1.

Table 1: Specification design of the Modified Jones Reductor

Parts	Length	Diameter
Coloumn. (Tip)	40cm (4cm)	2.0cm (1cm)
Receiver.	13cm	2.5cm
Neck of the receiver.	3cm	NS19
Adaptor.	NS19	NS14.5cm
Taps at the receiver.		2.5cm

The constructed Jones reductor was then tested in the Laboratory using Iron solution, to ascertain that it function well.

### Packing of the Column

About 300g of granulated zinc was weighed. 1M HCl solution was prepared and added to the weighed zinc till it was covered. The whole system was stirred and the acid decanted. 25%  $HgCl_2$  solution was prepared and added to the zinc after the acid was decanted, and then stirred for 5-10minutes. The solution was decanted and the zinc amalgam washed three times with distilled water by decantation. The amalgam was then put slowly into the column with vibration until the required packing was achieved. The column was vibrated for a long time to allow the amalgam settle uniformly. After which water was passed through the column and stored until put in use, in such a way the column was always covered with water to avoid contact with atmospheric oxygen. Before used, the column was reactivated with about 50ml of 1M HCl, the acid then drained slowly until it fell just above the zinc level, then

the tap was closed. This was repeated twice and finally washed with water. Before starting the work, a test reduction was done using  $\text{Fe}^{3+}$ . The quantitative reduction of the  $\text{Fe}^{3+}$  was tested by titrating against  $\text{KMnO}_4$ .

**Table 2: Equipments used**

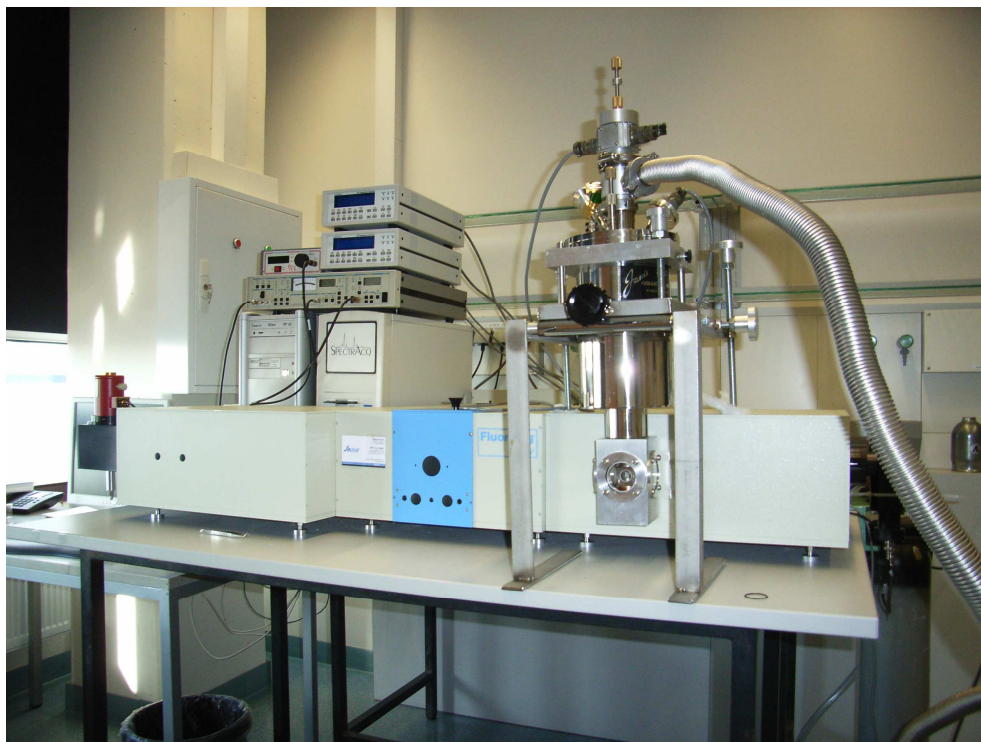
Equipment	Company
Argon glove box	Braun [Germany]
Fluorolog <sup>®</sup> -3 spectrofluorometer, FL3-22	Jobin Yvon [USA]
Liquid nitrogen cryostat, VNF-100	Janis research [Wilmington, MA]
Powder diffractometer D5000	Siemens [Germany]
Imaging Plate Diffraction System, IPDS	STOE [Darmstadt, Germany]
IFT-IR Spectrometer, IFS 113V	Bruker [Karlsruhe, Germany]
Vacuum Pump	ILMVAC GmbH [Germany]

### Reduction of Europium ( $\text{Eu}^{3+}$ ):

$\text{EuCl}_3$  was used in this work as the source of Eu ion. 0.05% M of  $\text{EuCl}_3$  was dissolved in water and used for the reduction. The water used was degassed by boiling it to expel  $\text{O}_2$  and then nitrogen gas bubbled into it before use. The receiver was dipped into a beaker containing water, and then the water was slowly heated to  $60^\circ\text{C}$  while stirring to allow for uniform temperature distribution on the receiver. One arm of the receiver was connected to inert gas ( $\text{N}_2$ ) and the other, to the vacuum. Before the solution of  $\text{EuCl}_3$  was put into the reductor, the arm connected to inert gas was opened to float the system with  $\text{N}_2$  so as to expel  $\text{O}_2$ . The flow of the inert gas was maintained during the reduction. The solution was then slowly passed through the reductor at the rate of  $\approx 0.4 - 0.6\text{ml/min}$ . After the completion of the reduction, the arm to inert gas was closed and that to vacuum opened. The reduced sample was removed under inert gas, closed and taken into the glove box and prepared for luminescence measurement.

### Measurement of Luminescence Spectra

The luminescence measurement was done using a Fluorolog-3 (FL3-22) spectrofluorometer from Jobin Yvon (fig. 3). This spectrofluorometer is equipped with a 450w xenon lamp, two double grated monochromators for emission and excitation. It also contains a photomultiplier with a photon counting system. The measurement procedure is as follows:- The cryostat was evacuated for about 15minutes and then floated with  $\text{N}_2$  gas, then cooled down to 80K using liquid nitrogen cryostat. After cooling the heater was started and the sample intensity adjusted to obtain maximum intensity possible. The spectra were then measured using DATAMAX computer program and the obtained spectra drawn using the computer soft ware Origin 6.0. During measurement emission spectra was corrected for the photomultiplier sensitivity.



**Fig 3 Fluorolog-3 (FL3-22)**



**RESULTS AND DISCUSSION**

The Jones Reductor constructed in this study is shown in fig 4 below with the main modification being on the receiver. In constructing the Reductor, it was taken into consideration that the reduced Europium (Eu) has to be doped immediately into the host lattice. In view of this the traditional volumetric flask or filter flask commonly used would not be suitable. The receiver was modified to be wide enough to allow for the removal of the dried doped compound. The major precaution taken was the prevention of oxygen into the reduced Eu solution, during reduction and doping. This was achieved by constructing two stop-cocks on the receiver, one to inert gas and another to vacuum. A small adaptor was placed between the receiver and the column, which could easily be closed after the sample was ready, to still prevent oxygen into the sample during removal. This modification can be compared with those already discussed in the literature, since all the modifications were done on the receiver to fit into the intended works, and the column have always remained the same.



**Fig 4. The Constructed Modified Jones Reductor**

As in Edwards work [11], the receiver was modified to be suitable for the reduction of hot or warm samples, by fitting it into a cooling system. Similarly, in the study by Taeb [10], only the receiver was modified in the Jones reductor to enable a definite and constant rate of flow. Therefore, the modification on the Jones reductor in the present work is in good agreement with previous studies.

**Reduction of  $\text{Eu}^{3+}$  :**

$\text{Eu}^{3+}$  was reduced using the constructed Modified Jones reductor. The emission spectrum of  $\text{Eu}^{2+}$  ions was measured. The spectrum (fig 5) did not show any peak from  $\text{Eu}^{3+}$ , implying that  $\approx 100\%$  reduction was achieved. The peak at  $24570\text{cm}^{-1}$  (407nm) could be due to a  $4f5d-f$  transition of  $\text{Eu}^{2+}$ , or due to Raman water emission. Another peak seen at  $17667\text{cm}^{-1}$  (566nm) can be assigned also to  $f-d$  transition, but this is not sure. It could as well be some impurities. The main aim of this analysis is to detect if  $\text{Eu}^{3+}$  is inside, which did not appear. This result gives us the reduction efficiency of the Reductor. The problem of re-oxidation was avoided, since there was only a small time laps between reduction and measurement.

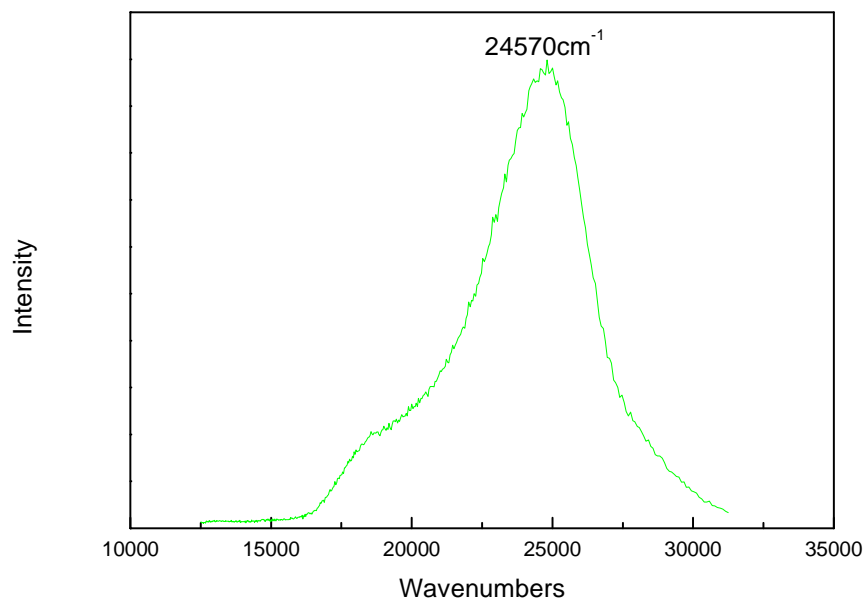


Fig 5: Emission spectra of Eu<sup>2+</sup> in water.  $\nu_{ex} = 35714\text{cm}^{-1}$  T = RT

### CONCLUSION

In this work a modified Jones Reductor, suitable for reduction and doping Europium into thermally unstable host lattice was successfully constructed. The modified Jones Reductor was used to reduce europium in solution and was found to be efficient since  $\approx 99\%$  reduction was obtained. Thus the constructed modified Jones Reductor can be successfully used for reducing and doping europium into thermally unstable Host lattice.

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