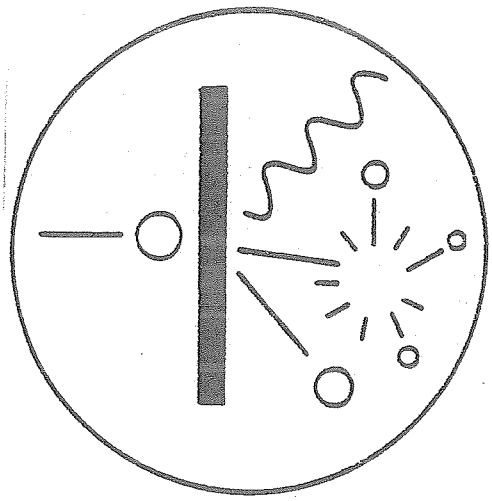
INTERNATIONAL NUCLEAR

TARGET DEVELOPMENT SOCIETY

NEWSLETTER



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International Nuclear Target Development Society
c/o Mrs Joanne M. Heagney
P.O. Box 123
Deer Harbor, WA 98243
USA
Tel: (360) 376-4007
Fax: (306) 376-5356

Editor: Chris Ingelbrecht
Institute for Reference Materials and Measurements,
Joint Research Centre,
European Commission
Retieseweg
B-2400 Geel, Belgium

Tel: +32-14-571-600
Telefax: +32-14-590-406
E-mail: Ingelbrecht@irmm.jrc.be

EDITOR'S NOTE

Dear Colleagues,

Very sadly, I have to report the death of Frank Karasek on 29 November 1996. There cannot be many INTDS members who did not know this modest and sincere man, who was a member of the society from the earliest days, and whose pioneering work on metal foils is still regularly acknowledged and referenced. A memorial to him appears in this Newsletter.

On a happier note, I wish you all a prosperous New Year.

Chris Ingelbrecht
Editor

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In Memory of Frank Karasek, 13 April 1924 - 29 November 1996

With sadness, we note the recent death of Frank Karasek. Frank was a longtime friend and valued professional counsultant of many targetmakers. His years of prominent service to the research community were acknowledged with an INTDS Award of Recognition in 1994. A scholarship fund has been established in his memory, at the request of Lil Karasek and their daughter, Sandy, and son, Scott. "Frank believed in education," Lil said recently. Indeed, he was a patient teacher and mentor. He also had an unsinkable disposition and a wonderful chuckle.

Frank's career at Argonne National Lab began in 1950, after he earned a college chemistry degree in night classes. He joined what later became Argonne's Metallurgy Department and grappled with finding ways to form experimental alloys into useful shapes. Without doubt, he became very good at it because he was enlisted to work on a string of landmark research projects. He was involved in the development of prototype clad-fuel elements for the EBWR: an acronym for the experimental boiling water reactor that was the prototype for US commercial power reactors. In the mid-1950s, he fabricated the metal cladding of the fuel rods for the first nuclear submarine. Later, he fabricated niobium into magnet coils for the first superconducting linacs. For an experiment on one of the first space shuttle flights, he made many foils to exacting specifications

In the late 1950s, he began to make thin foils of separated isotopes for the physicists at Argonne. The methods for roll-thinning he developed brought an invitation to present a paper at the Second Symposium on Research Materials, sponsored by the AERA in Harwell, England in 1965: seven years before the first INTDS meeting. He also presented a paper at the Third Symposium, sponsored by ORNL in 1971, and of course he made significant contributions at INTDS conferences. These remain a valuable introduction to his techniques.

In 1967, officials at Argonne decided that Frank's time and the government equipment should not be used to supply foils for research beyond Argonne's research mission. Thus, in the evening hours his basement grew into Microfoils: a one-man business in which making a profit was far less important than meeting research needs. Frank retired from Argonne in 1990 with the title of Engineering Specialist and more than 40 years of service. Throughout his years there, he was an acknowledged expert called upon to work with refractory alloys and a host of other nearly intractable materials. After retirement, Frank continued to work full time at his business, supplying the world with "state of the art" rolled foils, custom alloys and other fabrications. In the spring of 1996, progressive illness finally halted his efforts.

Lil said their children and grandchildren joined them for a wonderful Thanksgiving this year. The following day Frank had heart failure in his shop, where he loved to work. We will miss him.

Those who wish to contribute to the INTDS Frank Karasek Memorial Fund may send a donation to the INTDS Corresponding Secretary and Treasurer, Joanne Heagney.

WRL and JMH

INTDS Award Presentation to Jean Pauwels, Obernai, France, 9 October 1996

Tonight we have the pleasure of presenting a well-deserved recognition award to Jean Pauwels. In 1994 Jean suffered a promotion and became head of the Management of Reference Materials Unit at IRMM. It seems Jean cannot run as well as he can jump. One would expect the athlete who won second in the Belgium High Jump Championship in 1957, to escape such a fate. In any case, the INTDS lost a star contributor.

Many of you were in Garching, in 1978, attending the 7th of these conferences. That was Jean's first, and he was an author of three papers. For two, he was first-author and presenter. One of these was a solid treatment of spray-painting actinide deposits, and the other was amazing; We learned how to prepare films of polyimide as thin as 12 $\mu g/cm^2$. Since 1962, the Dupont Company had marketed these films of Kapton with a minimum thickness of 1000 $\mu g/cm^2$. In the scientific literature, no one had published a method to make the films in *any* thickness. I can remember thinking "Who *is* this guy?"

Eighteen years later, here is part of the answer: In 1968, Jean Pauwels earned a PhD in chemistry from the University of Gent. In preparing his thesis on the preparation of lithium isotopic mixtures, he had worked in Geel at the Central Bureau for Nuclear Measurements. Beginning in 1969, for six years he was employed by Eurisotop in Brussels, working on the analysis of gases in nonferrous metals. In 1975, he returned to Geel and worked with Jon Van Audenhove on target preparation, mainly doing chemistry and making thin layers.

Tonight we can only touch on the meaningful contributions he has made in more than 122 publications. The breadth of his expertise may be found in more than thirty contributions to INTDS publications: They denote extensive development work to prepare and characterize films of many plastics, vacuum-evaporated layers, sprayed layers, special targets of actinides and stable isotopes, and methods to gain precision thickness measurements.

Jean was one of the pioneers of solid sampling Zeeman Atomic Absorption Analysis for homogeneity control. He instigated the creation of an IRMM neutron activation laboratory at the Belgian Nuclear Center. He was responsible for the development of the Community Reference Bureau (BCR) laboratory and associated installations for the preparation of biological and environmental reference materials. He was responsible for the commercialization of the Research Materials operation at Geel. Currently, he is a member of the Scientific Evaluation Group of the Community Reference Bureau, as well as the Standardization Measurements and Testing Regulatory Committee. He is also a member of the ISO Reference Materials Committee and an organizer for BERM conferences on reference materials, and for conferences on solid sampling.

In 1984, Jean co-hosted the 12th World Conference of the INTDS, co-edited those proceedings, and has served admirably on the Board since 1988. He has been spared the opportunity of serving as our president, but until he jumped from our grasp, he was, as we say, a marked man. Thank you for joining us tonight, Jean. We are delighted to present this award to you.

WRL

Reflections on the 18th INTDS World Conference

Andree Méens, her staff, and the Local Organizing Committee are to be congratulated for an exceptionally well organized, educational, and enjoyable conference — right down to the product literature displays. Behind the scenes, she and her team were commendably successful in enlisting travel support funding which helped a number of presenters to attend. The participants were from 22 countries, which is, I believe, an INTDS record.

The conference was dedicated to Ed Kobisk and Joe Gallant. Both were instrumental in forming the INTDS and in shaping its nature. After CRN Director Bernard Haas welcomed us to CRN, he offered a personal tribute to Joe and told of an occasion in which Joe had given a warning about the possibility of a contaminate appearing in a target because of the backing chosen for it. The warning was remembered and wryly appreciated when odd lines appeared in spectra. He also warmly reflected on his friendship with Joe, which began many years ago at Chalk River.

Although Peter Dmytrenko was unable to attend as he had planned, he provided a written historical review of the target-making facilities at Chalk River, to be read to the attendees. It contained, in good measure, a summary of Joe's contributions.

Harold Adair, now retired from ORNL, presented a corresponding historical review for ORNL. Ed's contributions there were even more remarkable and lasting than perhaps most of us realized.

The text of these historical reviews/tributes will appear in the proceedings of the conference. Ed and Joe's professional accomplishments are inspiring; So too are our memories of their unpretentious, friendly personalities.

A valuable introduction to the history and current interests of the Workshop on Targets and Target Chemistry (WTTC) group was presented by Frank Helus and Thomas Ruth. The three medical-isotope-related presentations which followed were well received. The hope and expectation is that cooperation between the WTTC and the INTDS will continue in future conferences.

Andree was worried that "Mr. Murphy" might attend. Most certainly, he did not. On behalf of the lucky attendees, I sincerely thank Andree and CRN for a great conference!

Bill Lozowski
President, INTDS

Hydrogen Reduction of Metal Oxides to Metals and their subsequent Rolling to Target Foils

S. Clifford*, Xu Guo Ji†, C. Ingelbrecht, M. Pomeroy*

Institute for Reference Materials and Measurements
Retieseweg 9, B-2440 Geel, Belgium.

1. Introduction

Hydrogen reduction is a useful and widely used technique for the preparation of small quantities of various elements for use in the preparation of accelerator targets.[1,2,3] the method is restricted to a limited range of elements, but generally gives a very clean product with high yield, which is particularly important in the case of high value stable isotopes.

2. Theory

Hydrogen reduction is usually carried out according to the following equation.

$$2n\ H_{2(g)} + M_mO_{2n} = 2n\ H_2O_{(g)} + mM_{(s)}$$

The equilibrium constant will then be

$$K = \frac{p_{H_2O}^{2n}\ \ a_M^m}{p_{H_2}^{2n}\ \ a_{M_mO_{2n}}}$$

Assuming that the original oxide and product metal are pure, the activities may be assumed to be unity. Therefore the equilibrium constant becomes

$$K = \left(\frac{p_{H_2O}}{p_{H_2}}\right)^{2n}$$

The Gibbs free energy is related to the equilibrium constant by the following relation

$$\Delta G = -RT\ln K$$

$$\Delta G = -RT\ln\left(\frac{p_{H_2O}}{p_{H_2}}\right)^{2n} \qquad \text{.....(1)}$$

For the purpose of plotting the $\log\left(\frac{p_{H_2O}}{p_{H_2}}\right)$ versus $\frac{10^4}{T}$ we calculate the values taking the balanced equation with one mole of hydrogen in each case (2n = 1). This means that one mole of hydrogen is involved in each reaction for which the thermodynamic data is calculated, and this allows comparison between the reactions (especially in terms of difficulty).

*University of Limerick, Ireland. †China Institute of Atomic Energy, Beijing , China.

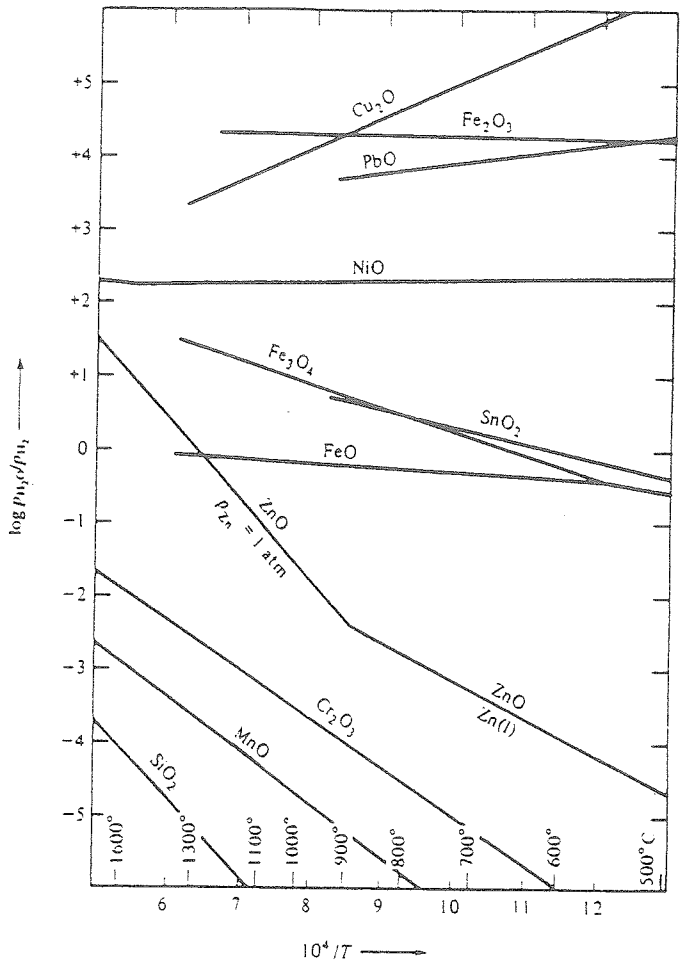


Fig 1. Equilibrium gas ratio $\frac{p_{H_2O}}{p_{H_2}}$ as function of inverse temperature for the reduction of various oxides.[4]

Using equation (1) with 2n = 1, the equation may be written in the form

$$\ln\left(\frac{p_{H_2O}}{p_{H_2}}\right) = -\frac{\Delta G}{R} \cdot \frac{1}{T} \qquad \text{.....(2)}$$

This equation is plotted in the above figure.

The $\frac{p_{H_2O}}{p_{H_2}}$ gives a measure of the extent of the reaction, i.e. the more water that is produced, the further the reduction reaction has progressed towards completion. This value also gives a measure of the amount of water that may be tolerated in the atmosphere before oxidation of the product metal occurs. For example, the ratios for the Cr_2O_3 reduction are very small (between 0.000001 at 600°C and 0.01 at 1600°C) which means that the furnace used here does not give temperatures high enough for the reduction reaction of chromium oxide to go to completion. If the water content of the hydrogen used cannot be maintained at extremely low concentrations then the reduction is not practical with this apparatus. From Fig. 1, the reduction of Cr_2O_3, MnO and SiO_2 are not practical with this system. The reason for this is due to the fact that flushing the system with hydrogen during reaction will not reduce the $\frac{p_{H_2O}}{p_{H_2}}$ ratio below the required value for complete reduction.

3. Experimental Procedure and Results

The system consists of a tube furnace (max. 1200°C) fitted with a quartz tube and argon and hydrogen inlets. All the connections are standard vacuum flanges but the tube is not evacuated, but flushed with argon until the reaction temperature is achieved. Prior to heating, the sample is inserted into the tube by use of a stainless steel plunger. When the reaction temperature is achieved the hydrogen valve is opened and a flow of between 3 and 5 litres per minute of clean dry H_2 is allowed to flow. After cooling, the weight loss of the material is determined and compared with the expected oxygen content of the original material. The conditions for each element reduced are given in Table 1 and efficiencies in Table 2.

Table 1. Conditions applied for the reduction of various elements[1].

Compound	Reaction Temp.°C	Boat	Comments
CdO	350 - 245	Vitreous C	Low yield due to volatility
Cr_2O_3	1300 - 1500	Porcelain	Using liq. N_2 water trap
CuO	200 - 600	Vitreous C	
Ga_2O_3	500	Vitreous C or Quartz	
GeO_2	600 - 700	Vitreous C or Quartz	
Fe_2O_3	600 - 900	Vitreous C or Porcelain	
$Pb(NO_3)$	400 - 600	Vitreous C	
Tl_2O_3	300 - 325	Vitreous C	Oxide is volatile (not >325°C)
SnO_2	600 - 1000	Vitreous C	
WO_3	450 - 800	Quartz	

The hydrogen reduction of oxides is relatively straightforward but care must be taken when reducing Molybdic oxide[5]. Molybdic oxide (MoO_3) is highly volatile at 600°C (sublimes) and therefore the steps taken in the reduction must be carefully chosen. The Molybdic anhydride (MoO_3) must be reduced to molybdenum dioxide (non volatile) at low temperatures the prevent the sublimation of MoO_3.

$$MoO_3 + H_2 = MoO_2 + H_2O \qquad 550°C$$
$$MoO_2 + 2H_2 = Mo + 2H_2O \qquad 950°C$$

Zinc and cadmium are difficult to prepare by hydrogen reduction due to the high vapour pressures of the metals.

4. Rolling

The method of pack rolling is used for foil preparation[6]. The stainless steel pack is prepared from 0.5 mm thickness highly polished stainless steel. The folded stainless steel pack is flattened by passing it trough the rolls. When the sample is in place the pack is rolled slowly at first with little compression and the sample is turned and rotated regularly to prevent the sample from cracking and sticking to the stainless steel. The gap between the rolls is decreased slowly and the sample continuously passed through reducing the thickness with each pass. Great care must be taken especially with indium, lead and tin which are very soft and bond strongly to the stainless steel. To help prevent this, when a pack is not yet finished (e.g. rolled to 50% completion), it now has a much smoother surface and this pack may be used later when the sample is thinner and a smoother pack is required. This pack will then be extremely smooth and may be placed inside another pack to continue rolling the sample to lower ultimate thickness. The results of the rolling are presented in table 2.

Table 2. Reduction efficiencies and foil thicknesses acheived.

Oxide → Metal	Temp. (°C)	Time (min)	Efficiency (%)	Foil thickness ($\mu g\ cm^{-2}$)
$CuO \rightarrow Cu$	700	120	99.8	450
$In_2O_3 \rightarrow In$	700	120	99.5	3500
$SnO_3 \rightarrow Sn$	700	120	99.8	3200
$PbO \rightarrow Pb$	500	60	99.9	4900
$GeO_2 \rightarrow Ge$	700	105	99.4	
$WO_3 \rightarrow W$	900	120	99.9	
$Fe_2O_3 \rightarrow Fe$	700	150	99.8	390
$NiO \rightarrow Ni$	700	60	99.5	300
$Co_2O_3 \rightarrow Co$	700	60	99.7	
$MoO_3 \rightarrow MoO_2$	550	60		
$MoO_2 \rightarrow Mo$	950	60	99.5	

5. References

1 Heagney, J.M., Heagney, J.S.
Reduction Techniques for Isotopic Materials
INTDS 5th World Conference, 1976.

2 Caudhill H.H., McBride L.E., McDaniel E.W.
Concurrent reduction and distillation - an improved technique for the recovery and chemical refinement of the isotopes of cadmium and zinc.
Proceedings of the 11th world conference of the International Nuclear Target Development Society, 1982.

3 Dushman S., Lafferty J.M., 1962
Scientific Foundations of Vacuum Technique
John Wiley & Sons.

4 Terkel Rosenquivst
Principles of Extractive Metallurgy
McGraw Hill, 1983.

5 Quarrell, A.G., 1961.
Niobium, Tantalum, Molybdenum and Tungsten.

6 Karasek F.J.
Fabrication of ultrathin metallic foils
AERE Report - R5097, 1965.

Ta Crucible Design, Construction and Application to Metal Oxide Reduction

S. Clifford*, Xu Guo Ji*, C. Ingelbrecht, M. Pomeroy*.

Institute for Reference Material and Measurements
Retieseweg , B-2440 Geel, Belgium.

* University of Limerick, Ireland. * China Institute of Atomic Energy, Beijing, China.

1. Introduction

Ultimately, good crucible design leads to higher yields and when coupled with well designed collectors, high yields become the norm. When preparing metallic samples of very expensive highly enriched isotopes, these high yields are essential. High yields may be achieved by ensuring that the crucible coupled with the collector form a well sealed unit to prevent the loss of expensive metal vapour during processing. Laser welding has been applied to the preparation of Ta crucibles which are resistance heated and designed in such a way that maximum heating is applied in the region of the crucible where the sample is placed. These design and construction techniques have resulted in the production of strong, re-useable crucibles.

2. Guidelines for crucible / reaction mixture compatibility - Literature survey

Crucibles may fail for various reasons but alloying with a component of the sample mixture or reaction products is the predominant cause. Solubility and reactivity problems become more prominent at higher temperatures[1].Therefore phase diagrams may be used to help check compatibility between the crucible material and the components of the reaction mixture. The main aspect of importance from the point of view of the phase diagram is to check solubility limits at different temperatures (formation of low melting point eutectics), formation of intermetallic compounds etc. thereby assessing the compatibility of the materials[2,3,4].

Table 1. Elements that are compatible with tantalum[1].

	M.P. (°C)	B.P. (°C)	Comments
Ba	710	1770	Wets most metals. No alloying.
Be	1283	2450	
Cd	321	767	
Cs	28	669	
Ca	850	1440	
Ce	799	3426	
Cr	1850	2600	
Cu	1083	2580	
Er	1530	2600	
Gd	1312	2700	Alloys with Tantalum
Ga	30	2250	Alloys with Tantalum
In	156	2000	
La	920	4200	
Pb	327	1750	Does not wet Tantalum
Lu	1700	1900	
Mg	650	1100	
Mn	1250	2100	Wets Ta
Hg	-38.9	356.6	
K	63.6	774	
Rb	39	688	
Sm	1077	1791	
Se	217	685	Spoils vacuum system
Ag	962	2212	
Na	98	883	
Sr	769	1384	Wets Tantalum. No alloying.
Te	449	990	Wets Tantalum. No alloying.
Tl	304	1460	Wets Tantalum. No alloying.
Th	1750	4790	
Sn	232	2270	
Yb	819	1194	
Zn	420	907	

For reduction-distillation of the Rare Earths, the oxide and the reductant metal are in intimate contact with the crucible. The product metal is produced and transformed to the vapour phase and condenses on the cooled collector where the temperature is too low for extreme reaction to occur. The system is therefore not exposed to large quantities of molten product metal where alloying may occur easily. Ta has been used successfully as an induction heated crucible for Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb and La reduction-distillation[5].

Plansee Metals Limited catalogue on Tantalum gives some data on the resistance of Ta to liquid metals[6]. It states that Ta is inert to most liquid metals up to very high temperatures. It is especially stable in liquid Cu and Cd, even at high temperatures, but is unstable in liquid Al, Ni, Fe and Co. The following data are also given.

Table 2.

Element	Pb	Ga	K	Li	Mg	Na	Bi	Zn
Stability limit (°C)	1000	450	1000	1000	1150	1000	900	500

3. Laser Welding

Laser beam welding offers many advantages for the production of refractory metal Components. Some advantages are that laser light provides high energy densities, can be used in room atmosphere with inert gas flow over the component. No electrode or filler material is required and very narrow precise welds with good mechanical strength may be achieved[7].

4. Crucible Construction

The crucible was designed in such a way that the components are easily assembled to produce geometry's that are technically easy to weld (i.e. butt-joints and T-joints). The electrodes and base are produced by guillotining and punching of 0.8 mm Ta sheet as shown in Fig. 1. The tubular section of the crucible is machined on a lathe to the dimensions shown in Figure 1. The welding is carried out with a Nd-YAG laser with a beam diameter of 0.6 mm. The pulse parameters are: peak height 55-60%, pulse width 5 mS, pulse rate 15 Hz, yielding approximately 240 watts of power. The work piece is rotated at a rate of 20° per second.

The geometry chosen is also easy to mount on standard water cooled electrodes and small currents are required to achieve high temperatures relative to many other designs. The crucibles have been used repeatedly without weld failure (sometimes more than 20 reductions per crucible). The limiting factor for the repeated use of the crucible is often related to alloying and also to bending forces applied to the crucible electrodes during clamping in the water cooled electrodes.

5. References

1 Ross K.J., Sonntag B.
High temperature metal atom beam sources.
Rev. Sci. Instrm. 66(9), Sept. 1995.

2 Moffatt W.G.
The Handbook of Binary Phase Diagrams.
General Electric Company, 1981.

3 Elliott R.P., 1965
Constitution of Binary Alloys, First Supplement.
McGraw-Hill Book Company, 1965.

4 Shunk F.A.
Constitution of Binary Alloys, Second Supplement.
McGraw-Hill Book Company, 1969.

5 Kobisk E. H., Grisham W. B.
Application of the Reduction-Distillation Method for Preparing High Purity Rare Earth Isotope Metals.
Proc. Of the 7th Rare Earth Conference.
Vol. 1. P 457. 1968.

6 Plansee Metals Ltd.
Tantalum (Product Catalogue).

7 ASM Handbook Vol. 6.
Welding, Brazing and Soldering, 1993.
The Materials Information Society.

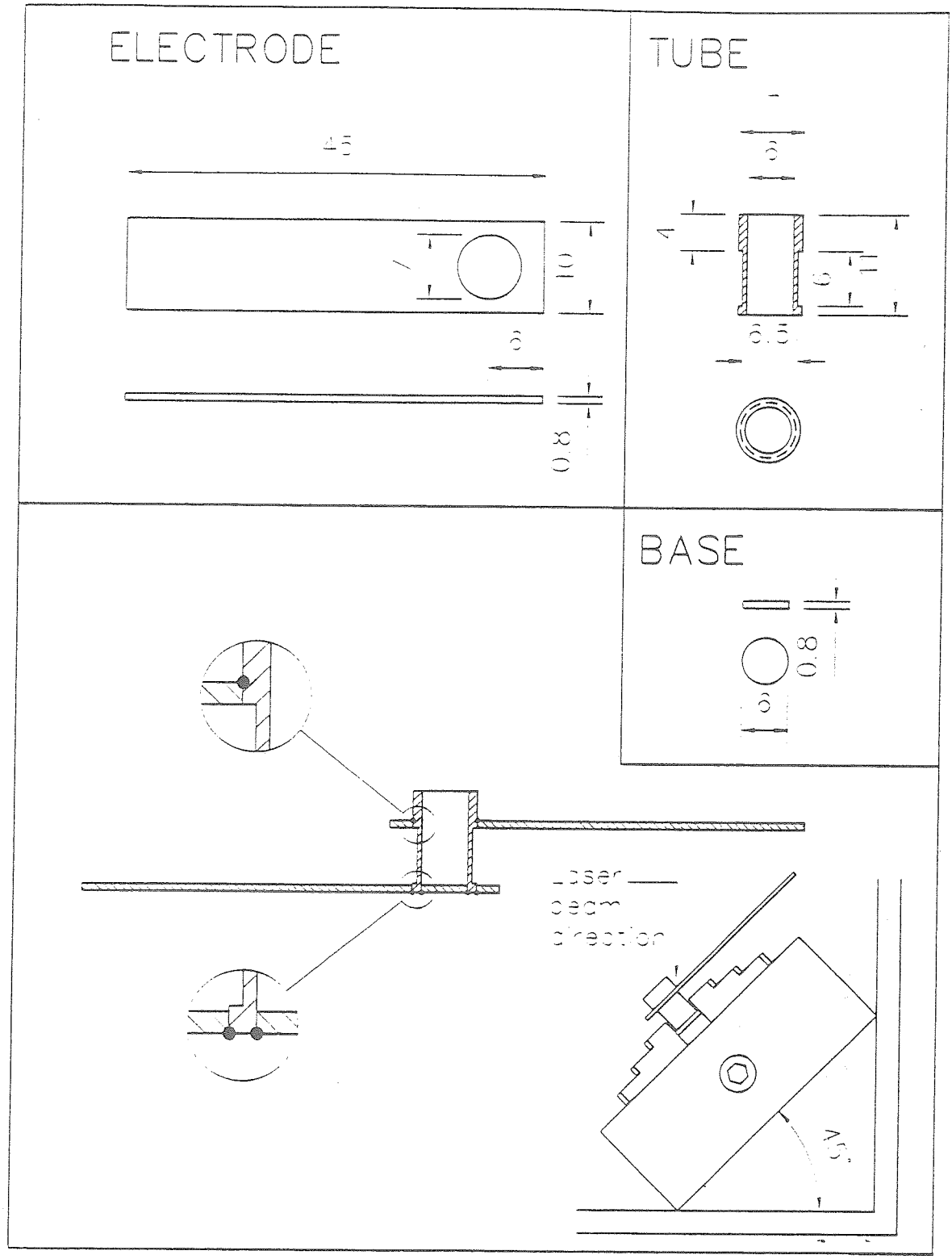


Fig.1 Tantalum reduction crucible

Reduction of Metal Oxides and Purification of Metals using Vacuum Evaporation and their Subsequent Rolling.

S. Clifford*, Xu Guo Ji*, C. Ingelbrecht, M. Pomeroy*.

Institute for Reference Material and Measurements
Retieseweg , B-2440 Geel, Belgium.

* University of Limerick, Ireland. * China Institute of Atomic Energy, Beijing, China.

1. Introduction

Methods for the preparation of various elements with high collection yields are given. The vacuum distillation method was designed in such a way that the crucible remains sealed during the distillation. This enables samples of higher purity to be obtained with relative ease. Electrolytic reduction was applied to zinc and cadmium and these samples were purified using distillation. The purity was determined by differential scanning calorimetry. The resulting metals from both methods were rolled into thin foils using the pack rolling method.

2. Reduction of oxide using resistance heating

Typically 150 mg of oxide was weighed, placed in a quartz boat and heated to 1000 °C. The weight loss is measured from time to time until constant mass is achieved. After this treatment the weight loss was found to be 0.5 wt.% for the rare earths and 34 wt.% in the case of MgO. The oxide is mixed with a 100 wt.% stoichiometric excess of reductant metal. The reaction mixture is ground with a mortar and pestle and pressed into a pellet.

A tantalum crucible that is specially prepared for these reductions is used[1]. The crucible is normally cleaned by pickling in concentrated nitric acid and then dried. It is then cleaned further by heating in vacuum to over 2000°C for 30 minutes between uses. The tightly fitting pellet is inserted into the crucible and a tantalum cap with a 1.6mm pinhole is placed very tightly on top (Fig. 2). A tantalum pin collector is mounted in a water cooled copper block. This collector set-up may be moved in the vertical direction and may also be rotated away from the crucible. This means that outgassing products and volatile impurities will not condense on the collector prior to reduction.

The crucible and pellet were outgassed at a temperature of between 500 and 1000°C depending on the oxide. The current to the crucible is increased gradually so that the outgassing is not too rapid. This may be monitored by the level of the vacuum. The pressure in the chamber is normally not allowed to increase above 10^{-4} mbar. The pressure decreases gradually when the outgassing is slower than the pumping speed of the vacuum pump and normally the pressure decreases very rapidly after completion of the outgassing. Further increases in heating current should not cause any increase in pressure when the outgassing is complete. This is a good indicator that the reduction is ready to proceed.

The reaction temperature is found indirectly by viewing the start of the deposition on a glass slide. This is done by using cheaper natural material. At this point the current input is noted and it is this value that will be used for the reduction evaporation of the isotopically enriched oxide. The current input may be increased to increase the kinetics of the reaction and also to increase the vapour pressure of the product metal. This range of temperature, when found to be suitable, is measured by optical pyrometry. This method is more suitable, for this type of reduction-evaporation experiments, than monitoring temperature alone because the evaporation rate is too sensitive to temperature. Small increases in temperature due to inaccuracies in measurement cause large increases in mass evaporation rate as shown for samarium in Table 1. Therefore the system is more controllable and repeatability of the experiment is higher using a stable power supply.

Table 1. Mass Evaporation versus Temperature for Samarium.

					increase	
M (Sm)	p^* / atm	p^* / Torr	T / K	Γ (Mass Evap. Rate)	Temp (%)	Evap. rate (%)
150.36	9.69E-06	7.36E-03	1000	1.67E-04 g cm^{-2} s^{-1}	-	-
	8.61E-05	6.54E-02	1100	1.41E-03 g cm^{-2} s^{-1}	10	750
	5.21E-04	3.96E-01	1200	8.19E-03 g cm^{-2} s^{-1}	10	4000
	2.30E-03	1.75E+00	1300	3.47E-02 g cm^{-2} s^{-1}	10	16000

The increase percentages are based on the values at 1000 K.

$\Gamma = 5.84 \times 10^{-2} (M/T)^{1/2} p_e$ g cm^{-2} s^{-1} M = Atomic Mass, T = Temperature, p_e = Vapour Pressure

The pin collector is rotated and moved down into position for reduction and evaporation of the sample to occur (Fig. 2). The metal collects on the cooled pin and forms a bead. The bead may then be removed by gripping the deposit and pulling it free of the pin. The results of these reductions are given in Table 2.

Table 2. Results of Reduction using Resistance Heating and Pin Collector.

Element	Reduction Temperature °C	Reductant	Collection Efficiency (%)
Sm	1250 – 1550	Hf	90
Yb	1200 - 1450	Hf	91
Eu	900 - 1150	La	92
Mg	1050 - 1350	Hf	91
Ca	900 - 1200	zr	92
Zn	700 - 900	C	90
Cd	600 - 800	C	95
Sr	900 - 1200	La	87
Cr	1500	Hf	90

3. Electrolytic reduction of Zn & Cd and purification by distillation

Electrolytic reduction is a convenient method for the production of Zinc and Cadmium. The resulting sponge metal is dried, pressed into a pellet and purified using vacuum evaporation using the set-ups shown in Figures 2 and 4. Figs. 4 and 5 show a collection method which can be used for the production or purification of natural material. In this case the initial quantity of material carries most of the impurities and also getters the residual atmosphere. This material also serves to seal the system so that none of the remaining residual gasses in the vacuum chamber can react or be incorporated into the sample.

The apparatus used for electrolytic reduction is shown in Fig 1. The platinum crucible is used as the anode and a polished stainless steel rod is used as the cathode. The following baths and conditions are used for reduction[4].

Zinc plating bath:

The zinc oxide sample is dissolved in H_2SO_4. NaOH is added until the onset of zinc oxide precipitation. The precipitate is re-dissolved using H_2SO_4. Reduction takes place with a current density of 4 - 8 mA/cm^2.

Cadmium plating bath:

The zinc oxide sample is dissolved in H_2SO_4. NH_4OH is added to adjust the pH to 5. Reduction takes place with a current density of 5 - 10 mA/cm^2.

The results are given in Table 3.

Table 3. Results of Electrolytic Reduction.

	Cd	Zn
Electrolytic Efficiency	98	90
Refining Efficiency	92.9	95
Overall Efficiency	91	85.5

The overall purity of the samples after vacuum refining was carried out using differential scanning calorimetry. This method utilises Van't Hoff's Isotherm to calculate the melt fraction of the sample. The result gives the melting point and the mole percent of the metal in the sample (Table 4).

Table 4. Results of Purity Measurements using DSC.

Element	M.P.(°C) Measured	M.P.(°C)Literature[5]	Purity (mol%)
Cd	321.61	320.9	99.99
Zn	420.43	419.58	99.98

4. Rolling of foils

The foils are rolled using the pack rolling technique[6]. This method is discussed in detail in Ref. 7. The results are given in Table 5.

Table 5. Foil Thickness achieved by rolling.

Element	Reduction Method	Thickness [mg/cm^2]
Sm	Distillation	0.17
Yb	Distillation	0.75
Eu	Distillation	4.2
Mg	Distillation	0.15
Ca	Distillation	0.35
Cr	Distillation	0.5
Zn	Electrowinning	0.6
Cd	Electrowinning	1.5

5. References

1 S. Clifford, Xu Guo Ji, C. Ingelbrecht, M. Pomeroy.
Ta Crucible Design, Construction and Application to Metal Oxide Reduction
INTDS Newsletter December 1996, vol. 23, no. 2.

2 R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, D.D. Wagman
Selected value of the Thermodynamic Properties of the Elements
American Society for Metals, 1973.

3 H.K. Pulker
Coatings on Glass
Elsevier, 1984.

4 J.M. Heagney, J.S. Heagney
Reduction Techniques for Isotopic Materials
INTDS 5th Annual Conference, Los Alamos, 1976.

5 Handbook of Chemistry and Physics
66th Edition, 1985 - 1986.
CRC Press

6 Karasek F. J.
Fabrication of ultrathin metallic foils
AERE Report - R5097, 1965.

7 S. Clifford, Xu Guo Ji, C. Ingelbrecht, M. Pomeroy.
Hydrogen Reduction of Metal Oxides to Metals and their subsequent Rolling to Target Foils
INTDS Newsletter December 1996, vol. 23, no. 2.

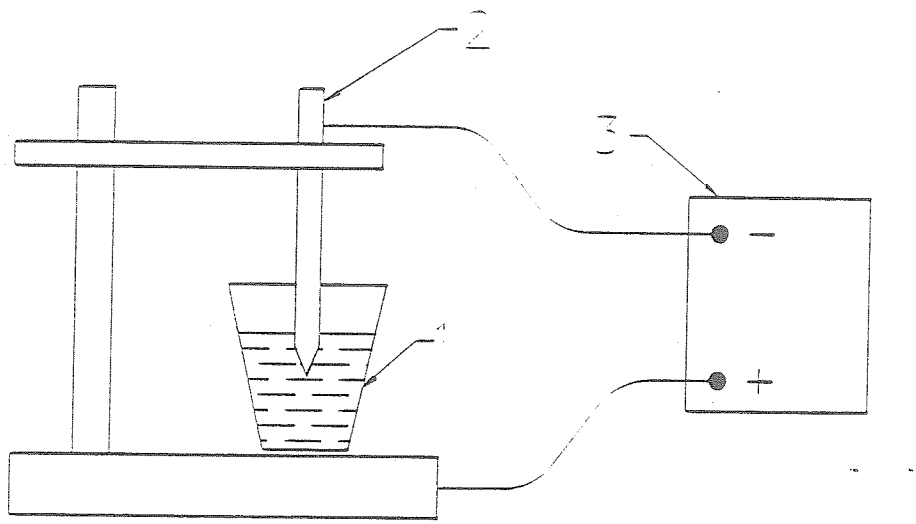


Fig. 1 Electrolytic Reduction Apparatus

Fig. 2 Pin Collector in the open position

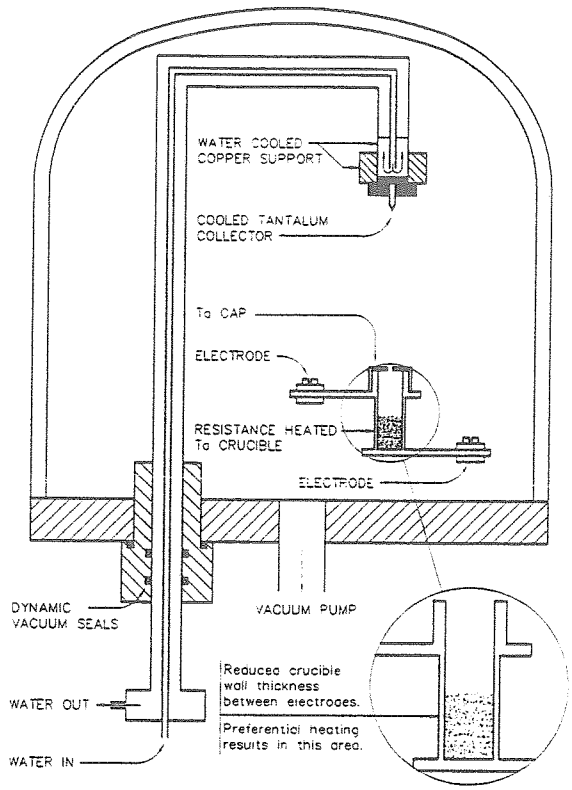


Fig. 3 Pin Collector in the closed position

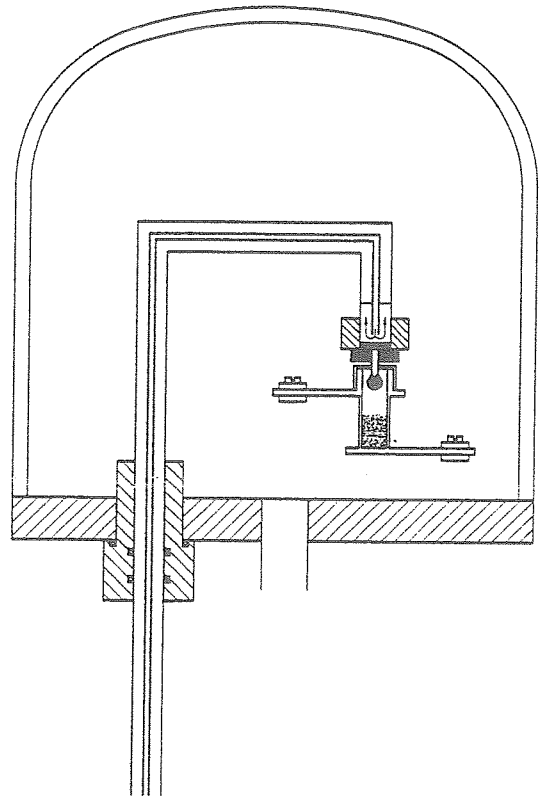


Fig. 4 Flat Cu Collector in the open position

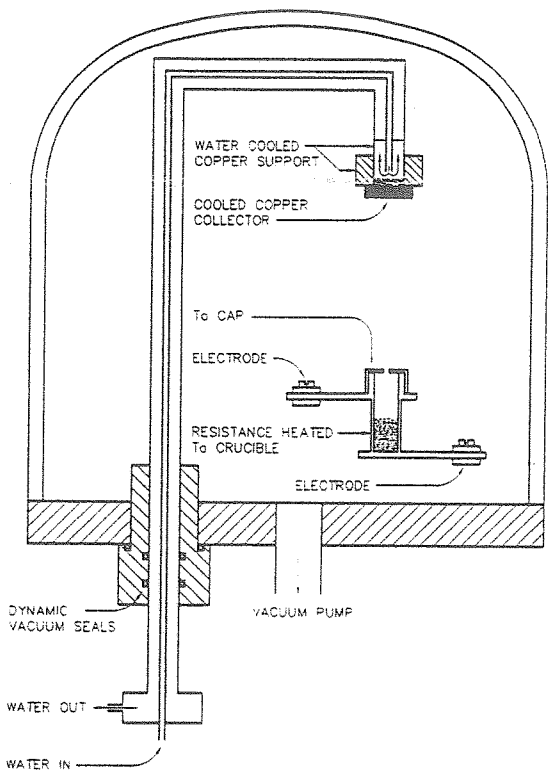
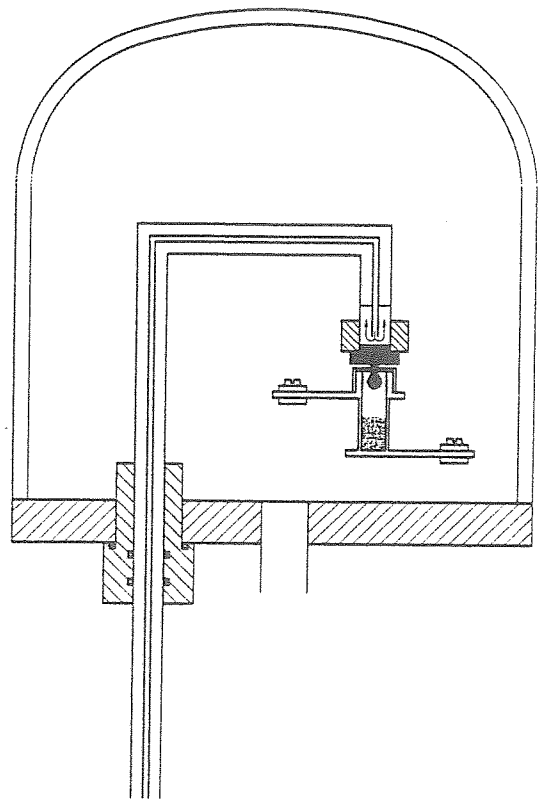


Fig. 5 Flat Cu Collector in the closed position



Application of reduction-distillation method for preparation of ^{144}Sm isotopic foils from a very small quantity of samarium oxide

A.R. Lipski
Nuclear Structure Laboratory, State University of New York at Sony Brook, Stony Brook, NY 11794-3800, USA

Abstract

Self supported targets of ^{144}Sm isotope were prepared from several milligrams of isotopically enriched $^{144}Sm_2O_3$. A vacuum reduction-distillation process for the production of high purity metal was followed by cold rolling.

1. Introduction

Due to a very high chemical stability of rare earth oxides, separation of a pure isotope requires proper preparation of the oxide, choice of the most effective reducing agent, a reduction and distillation procedure, as well as other materials (e.g. reaction vessel) and equipment necessary for successful operation. Several options have been discussed and presented in a number of references [1-3] which created a starting point for this application to a small amount (11 mg) of Sm_2O_3. The heating of the reaction mixture by the means of electron bombardment, used successfully in this laboratory for production of other isotopes from small amounts of compounds, seemed to be the most appropriate approach to the problem.

Overall yield reported for bigger oxide samples (20 mg - 200 mg) ranged between 80%-60%, depending on the collection method of the metal. Handling of samples should be reduced to a minimum, to help avoid losses. It is known that subsequent redistillation increases the purity of the metal (few percent - mostly contamination by reductant), but on the other hand, it significantly decreases the amount of useful isotope for further processing (rolling).

2. Procedure

A small amount of Sm_2O_3 (11 mg) was loaded into a ceramic crucible, then heated slowly with an acetylene torch in a hood in air, to drive off adsorbed water and carbon dioxide. A yellow, then yellow - brown smoke was observed to be released from the powder. Within a few minutes of the thermal treatment (the crucible became bright red) no smoke was observed, so the flame was turned off and the container with the load cooled down in air to room temperature.

A reaction container for the reduction was made from Nb tubing (2.5 mm diameter, 10 mm long) plugged on the bottom with a 3 mm long Ta rod and covered with a Ta cup on the other end. Sm_2O_3, a snow white powder, was transferred to the prepared reaction tubing and pressed with a drill for better thermal contact. A few pieces of La, freshly cut from an ingot (15 mg total weight, rather than powder used elsewhere) and cleaned of residual oil were inserted and pressed into the niobium tubing on the top of the oxide. The tubing was covered with a tight fitting Ta cup (to ensure good thermal contact with the rest of the container) with a hold of about 0.5 mm. The container was placed on the cooper base of the e-gun with a specially prepared insert and modified filament (fig. 1) in the vacuum bell jar. A polished, thick square Ta plate (2cm x 2cm, 3 mm thick) attached to a water cooled copper block was used as an isotope collector. It was found that the most effective collection of the metal takes place when the tantalum plate is positioned 1-0.8 mm above the cup of the reaction tubing. It was also determined that the cup should be 2-3 mm above the thermal-electrical shielding (fig. 1). The system was evacuated to $5x10^{-6}$ Torr. The filament current was increased slowly while observing vacuum fluctuations (never worse than 10^{-5} Torr) to ensure proper degassing of the sample up to the moment when further heating did not cause changes in the vacuum reading. At this point the temperature of the nozzle, measured with an optical pyrometer, was raised to 1400°C (lower part) and about 1200°C (the cup above shield). The reduction-distillation process takes place at this temperature and deposition of Sm can be observed on the condenser plate (this was done by using a dental mirror, fixed to the movable feedthrough). After deposition, which takes 3-4 minutes, power was turned off, the vacuum bell jar brought to atmospheric pressure with Ar and, after few minutes, opened. The deposit was checked under the microscope, removed (scraped) and weighed. 4.2 mg of metal was recovered (total yield 38%) but useful

pieces for pack rolling (described elsewhere [4,5]) were only 3.9 mg. Two foils 1.3 mg/cm² and 0.8 mg/cm² respectively were prepared with enough surface area to be mounted on frames (2x2 cm²).

3. Conclusion

This reduction-distillation procedure for small samarium oxide samples was successful in our case. The efficiency of the reaction might be increased by further miniaturization of the reduction source and avoiding additional handling by performing degassing in the same container.

References

[1] L. Westgaard and S. Bjornholm, Nucl. Instr. and Meth. 42 (1966) 77.

[2] E.H. Kobisk and H.L. Adair, Nucl. Instr. and Meth. 167 (1979) 153.

[3] R. Pengo, P. Favaron and G. Manente, Nucl. Instr. and Meth. in Phys. Res. A303 (1991) 152.

[4] A.R. Lipski, Nucl. Instr. and Meth in Phys. Res. A362 (1995) 98.

[5] A.R. Lipski, L.L. Lee Jr., J.F. Liang and J.C. Mahon, Nucl. Instr. and Meth in Phys. Res. A334 (1993) 126.

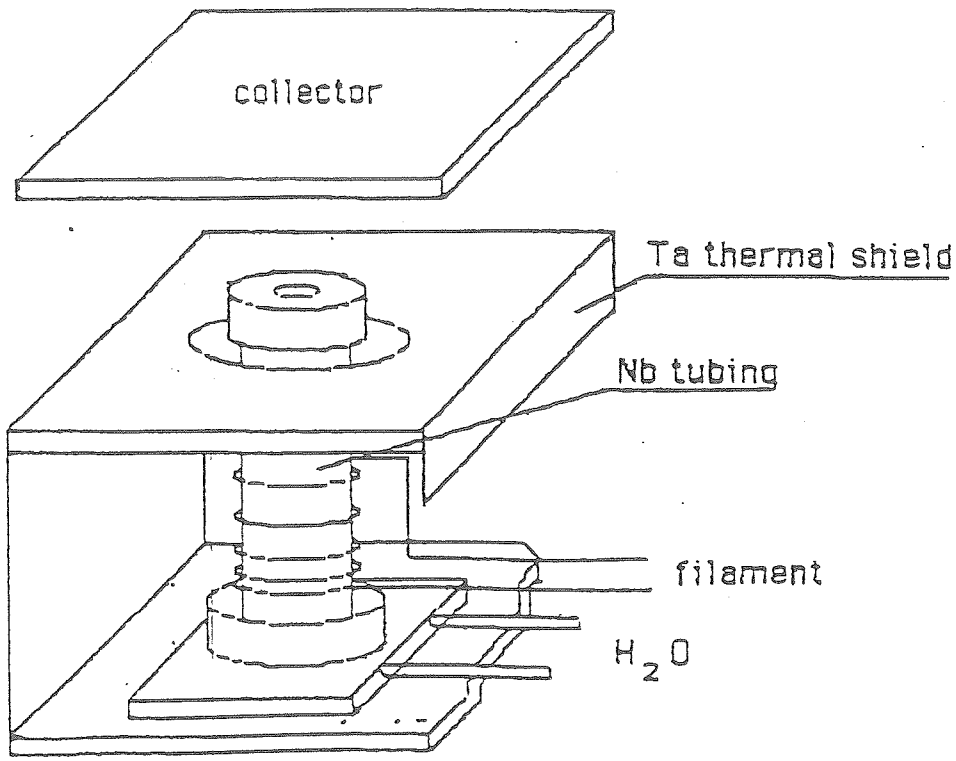


Figure 1. The insert for MRC V4-200 electron vapor deposition gun used