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ASSISTANCE TO THE BEIJING INSTITUTE OF CHEMICAL REAGENTS (BICR)  
IN THE PREPARATION OF HIGH PURITY CHEMICALS

DP/CPR/85/013/11-02

PEOPLE'S REPUBLIC OF CHINA

Technical Report: Mission from 31 August to 30 September 1987\*

Prepared for the Government of the People's Republic of China  
by the United Nations Industrial Development Organization,  
acting as executing agency for the United Nations Development Programme

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Consulting Chemist and Scientist

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Vienna

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## II ABSTRACT

Expert in preparation of high purity chemicals  
31 August to 30 September 1987

### A. Objectives

To strengthen Beijing Institute of Chemical Reagents (BICR) in order to enhance the national technical capability in all respects of research, development manufacture and application of Chemical reagents and fine Chemicals.

### B. Conclusions

The BICR is poorly equipment to carry out the objectives on their existing site. In early 1988 they will be moving to a new site which is better but lacks the clean working environment necessary to prepare very high purity reagents particularly for the Electronics Industry.

Their main work has been directed towards very few liquid reagents. In fact the main requirements are for very many different inorganic solids.

The staff lack the knowledge to carry out this work.

This report covers 28 days of my continued efforts to impart the practical methods of purifying elements and compounds from most members of The Periodic Table.

### C. Principle Recommendations

A chemist and a chemical engineer each at least 30 years experience in the High Purity Inorganic and Organic Industry is seconded to the BICR

Administrative assistance is required.

Additional inorganic chemists and marketing staff should be

employed.

Further training should be given to the staff by visiting High Purity Chemical Manufacturers from Europe and the USA.

Future work should include looking at the purification of the elements found in China.



### III. MAJOR RECOMMENDATIONS

Under each chapter recommendations are made in details. This briefly describe the major recommendation order of priority.

1. Second experienced chemist to BICR for at least 1 year.
2. Second experienced chemical engineer to BICR for at least 1 year
3. Purchase a better grade of raw material.
4. Employ chemists to find the market in China and elsewhere. Particularly visit Electronic Manufacturers.
5. Examine the resources of elements indigenous to China as potential high purity reagents.
6. Improve administration.
7. Improve library facilities.
8. Make strategic plan of work and carry it out.
9. Look for better quality raw materials.
10. Training programme must be carried out.
11. A very much cleaner working area is necessary.
12. Follow all recommendation indicated under Chapter IV on High Purity Reagent Preparations.
13. An experienced engineer and chemist from the High Purity Chemical Industry should examine the New Site plans.
14. Follow general recommendations on High Purity Products under Chapter VIII
15. Examine market requirements as indicated in Chapter IX and increase staff as required.
16. Large scale QMF type glassware should be made available.

## V INTRODUCTION

This report is the result of a visit made to the Beijing Institute of Chemical Reagents (B.I.C.R.) from 2-28 September 1987.

Briefing visits were made to UNIDO Vienna on the 31 August and 1 September 1987. De-briefing visits were made to UNIDO Vienna on the 29 and 30 September 1987. The object of the visit was to strengthen the BICR in order to enhance the national technical capability in all respects of research, development, manufacture and application of chemical reagents and fine chemicals.

The BICR (sometimes known as Beijing Chemical Reagent Research Institute) was established in 1958 as a part of the Beijing Chemical Works (BCW). It became independent in 1986 and occupies two buildings with approximate floor area  $500\text{m}^2$  each. A new building with floor area of  $6800\text{m}^2$  about 2.5km north west of existing site is being built and available in early 1988 for analysis, production, research and administration. The two older buildings may be used for organic work, but this is uncertain. BCW facilities are sometimes used on their site.

I spent about 8 hours at the BICR most days of my visit. I was well received and given a free hand to meet personnel and visit the working areas. Although provided with an interpreter, discussions were slow since the majority of the scientists did not speak English. In consequence progress was slow with difficulties and there may be some minor errors in this report due to translation difficulties.

The majority of my time was spent giving lectures with long discussions. Frequent visits to the laboratories to examine processes and advise on ways of improving the quality of the products. In addition advice was given on the preparation of many new high purity materials.

In particular advice was given on plant, packaging and the environmental condition necessary to prepare high purity reagents.

Both the new site and the old site were examined with great care.

## V STATE OF THE ART TECHNOLOGY IN BICR

### A. Existing Site

#### 1) Production of acid and solvents

The working areas are not clean, the extraction tends to be poor and draws in impurities. There is muc. cross-contamination. Corrosion is commonplace.

The operators, who do theis best, are not taught how to operate cleanly. The working areas are unsuitable for producing high purity materials.

#### 2) Research Development and Analytical

The analytical instruments are probably satisfactory but the working areas are not clean enough to carry out the analysis.

The impurities in the environment are probably for greater than the samples being analysed.

There is no criticism of the analyst's ability.

### B. New Site

It is very difficult to comment until this site is completed. I believe it will be better than the existing site.

I can already see many errors in the materials of construction. Undoubtedly positive air conditioning will assist.

### C. BICR Staff

The senior staff are indicated in Appendix 2. There is a cross section of chemists many with a strong bias towards analysis and organic chemistry. Their knowledge of theoretical chemistry is good as far I could judge. Those appeared to be a lack of practical knowledge in preparative high purity inorganic chemistry.

I am not suggesting that they were not competent chemists in their own fields of activity.

The term chemical engineer is frequently used but this does

not mean that they had formal training in chemical engineering as we would in the West.

D. Quality of products

The present output of 20-25 mainly liquid reagents would not satisfy the Western Electronic Industry since the analytical specifications are limited and do not include most of the metallic elements. It is possible that with additional analysis they may prove to be of acceptable quality.

E. Conclusion

There is much to be learnt in the art of purifying reagents to meet the stringent specifications required by the Electronics Industry.

## VI HIGH PURITY REAGENT PREPARATION

### A. Hydrochloric acid 36.5-38.5%

#### 1) General:

It is stated that 36.5-38.5% is distilled from commercial acid. This was not being prepared during my visit.

The still used for the preparation is similar to that used for nitric acid. (see B) The plant was not available for examination. The product is stored in borosilicate glass bottles and may be filtered through a millipore/Teflon filter if the particle size is high.

Distillation rate is 2 l/hour.

#### 2) Raw materials:

The commercial hydrochloric acid obtained is of exceptionally poor quality containing amongst other impurities:

Fe 2250ppm Mg 17 ppm Ca 17 ppm

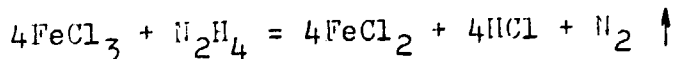
This is stated to be prepared by dissolving HCl gas in river water which contains impurities.

#### 3) Recommendations:

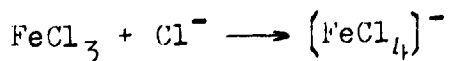
Attempts should be made to obtain a better quality raw material either by batch selection or requesting that the HCl gas is dissolved in pure water.

If the impurities are high the commercial acid should be distilled in a falling film evaporator and the gas absorbed in 20.22% HCl constant boiling azeotrope.

If the impurities are lower it may be simpler to treat with sufficient hydrazine hydrate to reduce the iron to ferrous chloride.



The acid is then passed through a anion exchange resin in the  $\text{Cl}^-$  form to remove impurities. If this is not carried out the iron may be present as the anion  $[\text{FeCl}_4]^-$  and will not be removed by the resin:



it may also be necessary to use a cation<sup>n</sup> resin in the  $\text{H}^+$  form

and As may be removed by reflux with powdered Cu or a little Zn.

Distillation is carried out by heating the acid in a quartz vessel fitted with a quartz fractionating column and condenser. The receiver is borosilicate glass. The issuing gas is dissolved into a previously distilled constant boiling mixture 20.22% HCl (bp<sub>760</sub> 108.5°C). The 36.5-38.5% HCl is removed from the receiver and the remaining acid is distilled to give 20.22% HCl for the next batch.

The product should be stored in clean borosilicate glass bottles after filtration which is only necessary when particle size is high. Filtration should not be necessary if cleanly distilled.

#### B. Nitric acid 69-71%

##### 1) General:

Commercial 95-100% HNO<sub>3</sub> is diluted to give 69-71% HNO<sub>3</sub> and passed through a millipore/Teflon filter. The acid is outgassed by passing clean air through the material and thus removing nitrogen oxides.

The acid is distilled from a 10 l quartz vessel fitted with a quartz vacuum jacketed fractionating packed column, reflux divider and condenser. The receiver is borosilicate.

Distillation rate 1 l/hour.

##### 2) Recommendation

The working area was not clean and there was a lot of corrosion. It is assumed when this work is removed to the new site greater use will be made of plastic or plastic coated materials.

Filtration of the final product should not be necessary.  
Purchase good quality raw material.

#### C. Hydrofluoric acid 40% and 50%

##### 1) General:

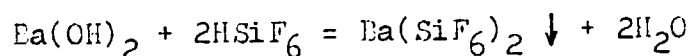
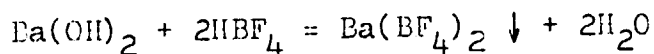
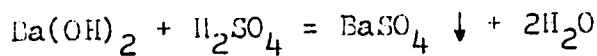
60% HF is diluted with water to 40% and heated in a silver vessel fitted with a Teflon fractionating column, condenser and receiver. Distillation rate is 1 l/hour.

It was stated that the major impurities were calcium, silicon, iron, boron and sulphate.

The liquid may be passed through a millipore/Teflon/cellulose filter before and after distillation. The product is stored in polyethylene bottles 50% is made by passing gas into 40%.

## 2) Recommendation:

Better selection of raw material. Pretreatment of the acid with an aqueous solution of barium hydroxide followed by decantation or filtration would help to remove some impurities



It is anticipated that the working area will be cleaner and greater use made of plastic and plastic coatings.

Purchase good quality raw material.

## D. Sulphuric acid 96%

### 1) General:

96%  $\text{H}_2\text{SO}_4$  is filtered and distilled under vacuum.

The acid is distilled under vacuum from a 10 l quartz vessel fitted with a quartz vacuum jacketed fractionating packed column, condenser and borosilicate glass receiver. Distillation rate is 1 l/hour.

The product is filtered through a millipore/Teflon filter and stored in borosilicate glass bottles.

### 2) Recommendation:

It is stated that frequent problems exist with the removal of impurities such as boron, fluorine and silica. This is most likely due to contamination by hydrofluoric acid being in the same working area. The hydrofluoric acid attacking the borosilicate glass contaminating the sulphuric acid with boron and probably silica

(not shown in specification).

The limit for B is 0.5ppm and it is suggested that the borosilicate glass receiver is replaced with quartz.

Filtration should not be necessary.

A cleaner working area would assist with purity.

Purchase better quality raw material.

#### E. Hydrogen peroxide 30%

##### 1) General:

30% pure raw material is purchased and passed through Teflon/cellulose/millipore filters to remove particles and stored in polyethylene bottles.

Although this was not being produced during my visit the area where general filtration was carried and was seen.

It consisted of a "clean" room which had rather badly corroded fittings.

##### 2) Recommendation

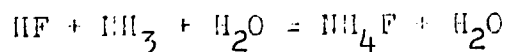
A very much cleaner area should be devoted to the filtration and packing of hydrogen peroxide.

#### F. Ammonium fluoride 40% solution

##### 1) General:

This is prepared in the same working area as the hydrofluoric acid.

Ammonia gas is scrubbed and passed into an aqueous solution of hydrofluoric acid until the pH is 6.2-7.0. This is carried out in a series of polyethylene bottles.



The solution is adjusted to 39-41% w/w, pH 6.2-7.0, passed through Teflon/cellulose/millipore filters and stored in polyethylene bottles.

##### 2) Recommendation:

It is surprising that the specification does not include Si



since I would suspect a high percentage. If this is high it may be reduced by preparing a strongly alkaline solution, allow to stand 24 hours and filtering. The pH may be adjusted by heating to remove the excess ammonis or adding further pure hydrofluoric acid.

The working area was untidy and badly corroded and it is anticipated that the extraction and working area will be improved on the new site.

### G. Ammonium fluoride 33.8-35.8% etchant

This is prepared in a similar manner to ammonium fluoride 40% W/W solution but has free HF 5.9-6.9%.

In fact it is a mixture of ammonium fluoride and ammonium hydrogen fluoride.

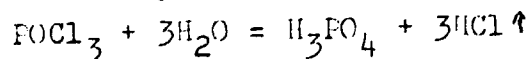
There is no Si in the specification which I suspect would be very high.

### H. Phosphoric acid 85%

#### 1) General:

Phosphorus oxytrichloride is fractionally distilled from a 5 l glass flask, fitted with packed glass vacuum jacketed fractionating column producing 3 l of pure material/day.

The pure phosphorus oxytrichloride is hydrolyzed with water and the HCl is removed by heating



About 2 Kg of phosphoric acid are produced each day.

The product is stored in borosilicate glass bottles.

#### 2) Recommendation:

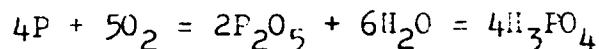
The apparatus should be all glass and not have the use of rubber bungs and many Teflon joints.

Alternative method are the use of phosphorus trichloride, a similar manner to phosphorus oxytrichloride.

Alternatively if yellow phosphorus were available this could be washed with cold dilute sulphuric acid and washed with water.

This could be followed by a further wash with cold sodium hydroxide solution followed with a water wash. (care  $\text{PH}_3$ )

Steam distillation should follow and the phosphorus should be burnt in air the phosphorus pentoxide, so formed, could be dissolved in water to give phosphoric acid



### I. Ammonium hydroxide 25% solution

#### 1) General:

Ammonia gas direct from a cylinder is scrubbed in a series of water traps and finally led into a bulk storage vessel containing pure water. The solution is filtered through a millipore/cellulose filter and stored in polyethylene bottles. All the apparatus was stated to be fabricated from polyethylene.

The plant was not available for inspection

#### 2) Recommendation:

The process should work satisfactory providing it is carried out in a clean area.

### J. Organic solvents

#### 1) General:

These are distilled from a 15 l stainless steel retort, fitted with a vacuum jacketed fractionating borosilicate glass column and water-cooled (15-18°C) condenser. Distillation rate is approximate 1 l/hour.

The only exception is trichloro ethylene which due its corrosive nature is distilled in the all glass apparatus similar to that used for nitric acid (see B)

Acetic acid is normally distilled in Room 118 in the analytical/research building using a similar glass apparatus to that described for nitric acid (see B).

Filtration is sometimes necessary through millipore/Teflon/cellulose and storage is in borosilicate glass.

The following solvents are purified:

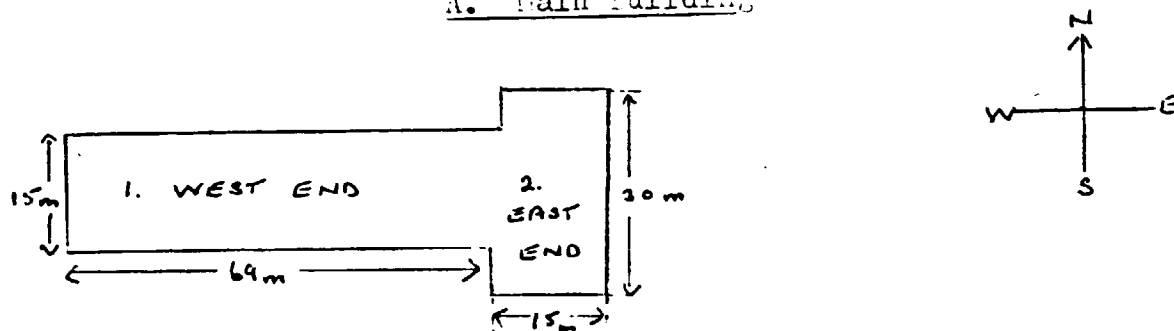
METHYL ALCOHOL  
ETHYL ALCOHOL ABSOLUTE  
ISO-PROPYL ALCOHOL  
ETHYLENE GLYCOL  
ACETONE  
TOLUENE  
XYLENE (MIXED ISOMERS)  
ETHYL ACETATE  
METHYLENE CHLORIDE  
TRICHLOROETHYLENE  
ACETIC ACID GLACIAL

2) Recommendation:

Greater care should be taken to avoid possible fire hazards, particularly where the solvents have low flash points. There should be no problem meeting the existing BICR specifications.

## VII NEW SITE

### A. Main Building



### MAIN BUILDING

This consists of two sections, situated about 2.5 km north west from the existing site and consists of:

#### 1) West End:

This has 5 floors, 1 st and 2 nd floor will be used for analytical instruments, 3 rd floor will be used for general chemical analysis. The three floors have air conditioning.

The 4 th floor will be used for general research and is fitted with extraction from fume cupboards. The 5 th floor mainly consists of extraction fans and water cooling, but there are two large offices. There is no air conditioning on either floor.

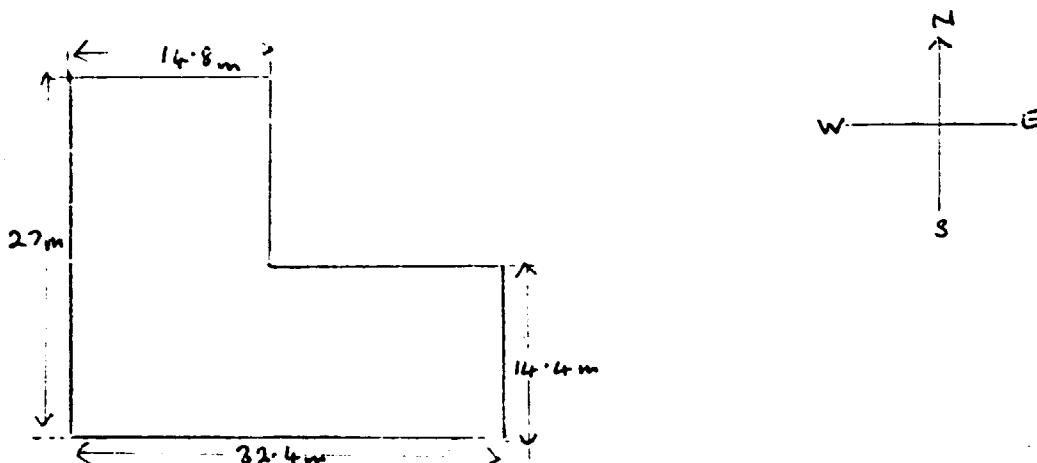
#### 2) East End

Consists of 3 floors. The 1 st floor is used for power distribution. The 2 nd floor is used for air conditioning plant.

The 3 rd floor is to be used as a lecture theatre which is estimated to hold 250 persons.

Toilet facilities are available.

### B. Inorganic Preparative Laboratories



This building is situated at south east corner of the site and consists of various laboratories for the following high purity preparation

1) Nitric, Hydrochloric and Sulphuric acid

Fume cupboard with extraction to take plant from existing site. There was a considerable amount of bare metalwork in bolts, pipework and grills to give contamination. by corrosion

2) Hydrofluoric acid

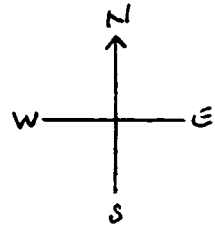
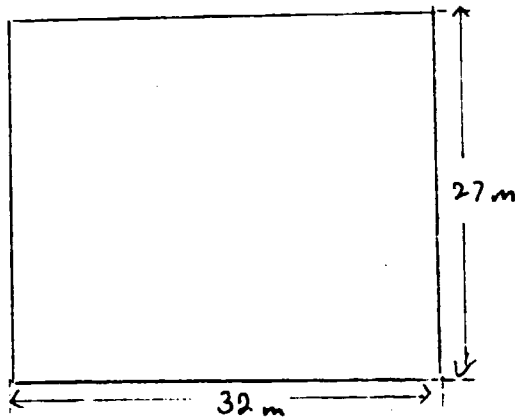
Fume cupboard to take plant from existing plant site with many exposed metal parts. It was stated that the fume cupboard were to be fitted with clear plastic. The windows to the laboratory are made of glass.

3) Organic solvents

This laboratory consisted of two similar fume cupboards fitted with many exposed metal fittings to take plant from the existing site.

It was felt that there were inadequate precautions for low flash point solvents.

C. Organic Preparative Laboratories



This was situated in the south west area of the site and consisted of several preparative laboratories with a central corridor. These were several PFOUDLER type vessels stated to be made in China. Some were glass lined and some stainless steel vessels ranged from 500-2000 l.

It is significant that stainless steel connections were made to glass lined vessels. This would undoubtedly cause problems when working with halides and free sulphuric acid.

The absence of any QVF type glassware is to be deplored.  
All standard services will be available.

#### D. Recommendation for New Site

Great care is taken to coat all exposed metal surfaces perferably with plastic type materials.

In the case of hydrofluoric acid eliminate any glass in the working area. Great care must be taken to avoid contamination from the environment and from personnel contact.

It is suggested that a competent experienced chemical engineer who is experienced in high purity chemical manufacture examines the plans.

## VIII GENERAL RECOMMENDATIONS ON HIGH PURITY PRODUCTS

### A. Raw Materials

It would make economic sense to purchase raw materials by batch selection based on analysis even if this makes the cost of purchase higher.

It would make processing cheaper and less laborious.

There is no reason why the BICR should not purchase high quality raw materials and possibly filter or carry out simple purification at a profit.

### B. Environment

All laboratories and plant examined were unsatisfactory for the manufacture of good high purity materials peeling paintwork, ledges where dust collected, corrosion of metal fittings left a lot to be desired.

The changing of footwear and overalls when entering a production or development area is very sensible.

It is suggested that some of the senior staff visit a clean rooms manufacturer either in the UK or the USA. Alternatively a manufacturer could be invited to Beijing to demonstrate. I have seen no area in the existing site which is suitable for the preparation of very high purity reagents.

Dust storms are common in Beijing and with the existing working conditions it would be impossible to avoid contamination.

The dust will carry silica, iron, calcium, magnesium and many other impurities.

Training must be given in this area.

The ideal area for working is similar to that of a hospital operating theatre, but without the antiseptics to contaminate the products. Account must be taken of corrosion.

### C. Health and Safety

Old fashioned fume cupboards with PVC ducting are adequate for extraction of fume.

The production areas for acids in general were messy with corrosive liquids on the floors. There was no evidence of protective clothing or eye protection being worn in any plant or laboratory.

It is strongly recommended that this is available and is seen to be used. Furthermore that training is given on health and safety.

#### D. Analytical Specifications

In general the standard of analysis is good. The specifications indicate between 5-14 metallic impurities to be examined at a very low level for each compound.

It is common practice with high purity materials to examine for almost every metallic element. These are summated and recorded as

TOTAL METALLIC IMPURITIES = tmi

In PARTS PER MILLION = ppm

i.e.  $tmi < xppm$

when x is frequently 1-10.

The present specifications are satisfactory if they meet the customer's requirements. If it is intended to compete with other suppliers then the specifications will have to include most metallic elements and some non-metallic elements.

#### E. Packing

This is carried by hand washing in de-ionised water followed by agitation in an ultrasonic vibrator. The bottles are drained on a plastic grill and pass to the production areas for packing.

There could be many improvements in this area. When possible packing should be carried out in the preparation area.

Automation of the packing and cleaning of bottles may be necessary when the output is large enough to warrant these methods.



F. Future Production Research and Development

The output at present relates to the preparation of a simple 20-30 high purity materials that are liquid at normal temperatures. The only exception are when preparing small research or development samples.

There is a vast number (several hundreds) of solid high purity materials that are used in the electronic industry and as primary standard in analysis. These are produced from most members of The Periodic Table.

The processing methods and plant are very different from liquid production. I have seen little plant on site to deal with these preparations.

There should be a much greater emphasis on inorganic research, development and production.

Most important of all, the elements which are indigenous to China should be examined. In particular the rare elements which are found in the country. Typically, platinum group metals, gold, silver, rare earths, tantalum, niobium, gallium, indium. The common elements such as molybdenum, tungsten, titanium, boron should not be ignored.

## IX MARKET REQUIREMENTS FOR HIGH PURITY REAGENTS

### A. Worldwide

It is not unusual for a chemical reagent manufacturer to have 10,000+ entries in their catalogues. They are not always different compounds, but there may be several grades of the same material.

The requirements can vary from a 100g to several 100kg but they are rarely required in tonnage quantities.

They are all of very high value. The value increases to a very high level as the purity increases independent of their intrinsic value.

If China is to compete with overseas trade it must have good market information and be prepared to carry out work on any compound from most of the elements. These remarks equally apply within China.

### B. Electronics Industry in research

Some information can be obtained by reading current journals.

The most up to date information is obtained by visiting electronic devices manufacturers and research institutions.

Discussion should take place with the physicists and material scientists. Always remember they do not always have an in depth chemical knowledge and may need guidance where purity levels are concerned.

The important thing to remember is that if the device works your material is satisfactory.

Most elements and their inorganic compounds are required. Some organometallic and organic compounds are also used.

### C. Primary standards

There is always a small but very valuable market for primary

standards used in instruments such as flame emission spectrometry.

The purity requirements are very high and include almost every element except those with short half-lives.

#### D. BICR reagents

These amounts to 20-25 liquid reagents mainly inorganic acid and many organic solvents. Their quality is only checked by a maximum of 30 elements as impurities. Some photoresist are prepared.

#### E. Quality control

The market requires that where possible high purity reagents are examined for most elements at very low levels.

#### F. Grade

There is no reason why more than one grade of a high purity material should not be solid eg

BEST GRADE AI	tmi	H.D. Use physical testing
GRADE 1	tmi	< 1-10 ppm
GRADE 2	tmi	< 11-100 ppm

#### G. Recommendation

BICR should be prepared to investigate the market, prepare a much wider range of primarily inorganic materials and examine for a wider range of elemental impurities.

## X LECTURES AND DISCUSSIONS

### A. General

Frequent round the table discussions were had with a wide variety of BICR staff. They discussed current problems. I gave them advice on how to deal with these and future problems. An average of 2-3 hours a day was spent on these subjects.

Six major lectures are given each lasting about 3 hours which included detailed discussions of recent and future problems.

I discussed the preparation and purification all elements, (except those with short half-lives) and many compounds.

I based the lectures on a paper I had previously given on the 2-4 th April 1986 titled "Production of Fine Chemicals for the Electronics Industry" publication no 60 by The R.S.C. London (see appendix 3).

The talks were slow since interpretation from English into Chinese was necessary.

Frequent questions were asked during the talks. Only a brief summation of the questions asked are mentioned.

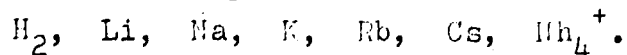
The numbers at these lectures and discussions varied from 10-60 personnel. Some chemists were also present from B.C.W.

I always emphasised that I was available at any time for discussions.

### B. Lecture 1.

#### 1) Talk:

I introduced the purity levels to make sure there was no misunderstanding of t.m.i. and ppm. Environmental contamination was discussed. Health and Safety was covered. In particular reference was made to batch selection and the fact it is frequently cheaper in the long run to purchase better quality raw materials. Purification of elements and compounds of the following were explained in detail:



2) Discussion:

The main questions related to the poor quality of their raw materials. How to purify HCl, NaCl, KCl etc.

It was a very intensive discussion but a certain reluctance to ask questions.

C. Lecture 2.

1) Talk:

Environmental and cross contamination was frequently stated. The necessity to work under cleaner conditions Materials of construction were explained. Purification of elements and compounds of the following were discussed in detail:

Be, Sr, Ca, Sc, V, La, Lanthanides

2) Discussion

This was very lively the audience seemed less reserved at asking questions

I dealt with a large number of questions relating to the purification of mineral acids. Several methods of analysis were discussed, in particular the examination of material for fiber-optic glasses.

Solvent extraction on the use of ion-exchange in relation to the Lanthanides was discussed in detail.

D. Lecture 3.

1) Talk:

Frequent reference was made to cross and personal contamination. The need to use plastics for construction or plastic coated metals.

Materials of construction for plant e.g. platinum, quartz, silver, borosilicate glass, Teflon plastics and many other materials for fabrications were discussed. Purification of elements and compounds of the following were explained in detail:

V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os.

## 2) Discussion

Solvent extraction was discussed particularly in relation to Hb/Ta. The various salts of V were discussed in detail

The preparation of finely divided metals was a frequent question and suggestions were made across a broad field.

The message was given that simple methods are very cheap and they should be tried before using complicated method or apparatus are used. In particular crystallisation and good filtration at every step.

## E. LECTURE 4.

### 1) Talk:

Repetition of the need to wash cleanly and select material for plant linings. The dangers of leaching impurities from plant linings Environmental contamination was also discussed.

Fractional distillation was discussed in detail. Purification of elements and compounds of the following elements were explained in detail:

Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Zn, Cd, Hg, B, Al, Ga.

### 2) Discussion

This was very broad and many questions were asked about metals of high intrinsic value. Methods of metal distillation and purification of the platinum group metals was prominent amongst the questions.

## F. LECTURE 5.

### 1) Talk:

Techniques such as zone refining, ion exchange resins and distillation were explained in detail.

Emphasis was placed on the purification of elements found in Chinese minerals and suggestion that this is an area which the BICR should concentrate. Purification of elements and compounds of the following were explained in detail:

In, Tl, C, Si, Ge, Sr, Pb, U<sub>2</sub>, P, As, Sb, Bi.

## 2) Discussion

Very many questions were asked concerning the chemistry of Si, Tl, In and rarer elements.

Frequent discussion in relation to toxicity were made. Apparatus and techniques not commonly used in the BICR were discussed.

## G. LECTURE 6.

### 1) Talk:

Electrolysis, difficult techniques and separations were explained

Purification of elements and compounds of the following elements were explained in detail

O<sub>2</sub>, S, Se, Te, F, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>, Th, U.

GASES, He, Ne, Ar, Kr, Xe.

A brief resume was given of the uses of organometallic compounds in the preparation of pure inorganic compounds.

In addition organic compounds were explained

A message particularly was given for the BICR to look at the many inorganic compounds used in the Electronics Industry. In particular look at the elements that are indigenous to China.

Methods of sampling was explained. The preparation electro-ceramic and superconductors was covered with some talk on photoresists.

### 2) Discussion

Very many questions on the future projects for the BICR were made. Clean rooms and techniques were discussed.

Availability of some raw materials were mentioned and it was suggested that a search for purer raw materials is made.

## XI APPARATUS AND PLANT

### A. Existing

#### 1) Development and Research Apparatus

By modern standard it is very old. Insufficient use is made of ground glass joints. Frequently rubber bungs are used, many joints are made with Teflon tubing.

I saw no proper glands on sealed stirrers

Fume cupboard were made of painted wood with PVC extraction ducts.

#### 2) Production

The largest flask I saw was 15 l although distillation apparatus were well set up there were many rubber bungs, plastic and Teflon joints.

#### 3) Analytical

I was given the impression that this was will equipped although many instruments were out of use. Some were outdated

### B. New Site

#### 1) Research; development and analysis

No apparatus was seen on the visit. It is anticipated that existing equipment will be transferred to the new site.

#### 2) Organic production

The plant installed was mainly Pfouder Type vessels, glass lined. It is significant that no large glass apparatus is anticipated. One stainless steel and one rubber lined centrifuge without covers were observed.

#### 3) Inorganic production

Fume cupboards were being built no plant was seen.

### C. Recommendations



It is suggested that QVF Type glassware is purchased and demonstrated, purchase wide diameter heat exchangers, larger flasks and isomantle heaters.

In particular join glassed lined steam jacketed vessels with glass joints and not stainless steel.

Visits to other manufacturers in USA, UK, Europe will give a better idea of the requirements.

China should be encouraged to manufacture large scale borosilicate QVF type glassware.

## XII QUALITY CONTROL

### A. Sample collection

#### 1) Present method

Samples are taken by the analyst from any laboratory producing the material.

The sample is transferred to the analyst's own container.

There is no method of storing the material in bond while being analysed or means to ensure that the sample represents the batch in question.

#### 2) Recommendation

Products should be held in bond and samples taken in the presence of the producer and only released after analysis.

It is preferable that the analyst takes the sample.

### B. Analytical specifications

A very much wider range of analysis to include most metallic elements should be carried out

In some cases non-metallic element analysis may be required.

### XIII EQUIPMENT AND STAFF

#### A. Objectives

It is stated in CP/CFE/85/013 that the immediate objectives are to strengthen the BICR in order to enhance the national technical capabilities in all aspects of research, development, manufacture of chemical reagents and fine chemicals.

This particularly applies to the Electronics Industry since the BICR requires considerable assistance in understanding the requirements of the Electronics Industry.

#### B. Organic Analysis

I found that the laboratories were well equipped with many new instruments, also there would appear to be some outdated equipment. The staff of 25+ appears to be high and they are competent chemists. There is a high proportion of staff with analytical training.

#### C. Organic Preparations

It is anticipated that on moving to the new site, better equipment will be provided.

The staff of 25+ appears to high and they are competent chemists.

#### D. Inorganic Analysis

The equipment on the Existing Site is poor. It is anticipated that it will improve on movement to the New Site. The staff of 10+ is inadequate.

It will be necessary to examine for many more elements than at present.

### E. Inorganic Preparations

Equipment is poor, clean room facilities are lacking. The staff of 22+ is inadequate. There would seem to be an apparent lack of knowledge in the preparation of high purity materials from the rarer elements.

### F. Health and Safety (Environmental Protection)

Greater attention needs to be paid to this area. A staff of 12+ is probably adequate. In particular the use of protective wear is very much lacking.

### G. Maintenance Staff

The present staff of 5+ is probably adequate, because many development personal assist in this work. Extra staff will be required as business increases.

### H. Sales and Marketing

To the best of my knowledge there is no person fully employed in this area. Permanent staff is urgently required who go out to visit the Electronic Industry to find out the high purity materials required.

### I. Management

The present staff of 12+ is adequate at present but may need to expand as the work load increases.

#### XIV TRAINING RECOMMENDATIONS

##### A. Literature

All staff should be encouraged to read up-to-date literature and all the standard journals in the electronics field should be freely available for consultation.

##### B. Lectures and Symposia

Staff should be encouraged to attend these lectures both inside and outside China. They should also justify their attendance and write reports of the meeting.

##### C. Clean Room and Laboratories

This can be achieved by visits to other chemical manufacturers. It is of little help to visit a "Hospital" clean room since they do not have the corrosion problems experienced in the Chemical Industry.

This will most likely require visits to the U.S.A., UK or other European Countries. There will be reluctance to allow chemists who are in competition to visit these works.

Perhaps in the U.K. on appeal to the Prime Minister (MRS.M. THATCHER) may help since like myself she is a Fellow of the Royal Society of chemistry (R.S.C.). I would suggest visits to the following in the UK:

— \* Johnson Matthey Chemicals Ltd., Royston, Hertfordshire.

— \* B.D.H. Chemicals Ltd., Poole, Dorset.

Royal Radar and Signals Establishment, Great Malvern, Worcester.  
University of Manchester Institute of Science and Technology.  
City of London University.

\* I used to work for both of these companies and mentioning my name may help or I can give assistance during visits. A request to the Royal Society of Chemistry, Burlington House, London may

also help, but mention my name.

#### D. Health and Safety

Knowledge can be acquired by visits to other companies. This is a very essential part of the training programme. Journals on health and safety must be obtained and read.

There should be no exceptions for wearing protective clothing.

#### E. Exhibitions

All exhibitions on the Electronics Industry should be attended and questions asked about the chemical requirements.

#### F. Works Visits

These should be encouraged and close contact made between chemists, physicists and material scientists involved in the fabrication of electronic devices.

#### G. Technical Assistance

This the most urgent of all the requirements. A Chemist and a Chemical Engineer with at least 30 years experience in the manufacture of high purity inorganic and organic reagents should be seconded to the BCCP for at least a year. It would assist if they had a good knowledge of administration in the Chemical Industry and could understand the Chinese language.

Training in marketing could be given by visiting experts.

#### H. Staff Requirement

It is suggested that the size of the Inorganic Staff be increased considerably since the Electronics Chemical Industry

requires many solid inorganic chemicals and elements.

In addition some chemists should be trained to carry out a marketing and sales programmes.

There is no point increasing staff unless the workload warrants extra numbers.

## XV LIBRARY FACILITIES

### A. Beijing Chemical Works

This library is available for the use of BICR personnel and is situated on their present site. I understand that at the New site BICR will not have a library but the ECW library will be available for use.

This library is not easily available for consultation and I only had a brief visit during my stay.

There was a wide range of Chemical Abstracts in English. Also several other older text books in English. It was not impressive.

Several volumes of Beilstein Organic Synthesis were available in German.

### B. Scientific Library of China

This is in the north west of Beijing at Zhong Guan Cun and about 20 Km from B.I.C.R.

I examined this library with great care and I impressed with its contents. Most of the scientific literature required by the BICR is available in many languages, principally in English and Chinese.

There was a very wide range of scientific journals available.

### C. Beijing Central Library

This old library is situated near BEIHAI PARK and is closed. A new library is being built near QIZHUYUAN PARK, north west Beijing and all the books are being transferred to this new library. It was closed during my visit.

I understand that the scientific content of this library is not very good.



#### D. Recommendations

That the BICR have a library of their own on the new site In particular they should have copies of standards works with the latest.

#### E. Donated Books

In order to assist to start the formation of a new library. I left the following:

- 1) FINE CHEMICAL FOR THE ELECTRONICS INDUSTRY (Royal Society of Chemistry Special Publication No 60)
- 2) SPECIALITY INORGANIC CHEMICALS (Royal Society of Chemistry Special Publication No 40)
- 3) THE MODERN INORGANIC CHEMICALS INDUSTRY (The Chemical Society Special Publication No 31)
- 4) ANALAR STANDARDS FOR LABORATORY CHEMICALS
- 5) BDH BIOCHEMICALS, DIAGNOSTIC, FINE CHEMICALS CATALOGUE
- 6) CHEMTRONICS (Putterworth)

Volume	1	No	1
Volume	1	No	2
Volume	1	No	3
- 7) VARIOUS CHEMICAL CATALOGUES
- 8) TEXT BOOK OF ORGANIC CHEMISTRY (Fieser and Fieser)

#### F. Recommended Books

- 1) Inorganic Synthesis (Wiley) Volumes 1-30+
- 2) Preparative Inorganic Chemistry G. Brauer English Language Edition 2 volumes
- 3) Organic Synthesis A. I. Vogel.

*L. P. Vergnano*  
(L. P. VERGNANO)

XVI APPENDIX 1.

DIARY

- 31 August 1987 04.00 hrs. Depart Home Poole, Dorset England  
August 1987 pm Arrived Vienna for briefing at UNIDO HQ
1. September 1987 am Briefing UNIDO Vienna  
pm Depart Vienna Frankfurt
  2. September 1987 pm Arrive Peijing meet BICR personnel
  3. September 1987 am Meet UNIDO/UNDP Officers  
pm At BICR discussion
  4. September 1987 BICR Laboratory tour
  5. September 1987 Prepare report
  6. September 1987 Prepare lecture
  7. September 1987 BICR Laboratory tour
  8. September 1987 BICR Lecture and discussion
  9. September 1987 BICR Discussion
  10. September 1987 Visit Scientific Library of China
  11. September 1987 BICR Discussion with Director and visit New Site
  12. September 1987 Prepare report
  13. September 1987 Prepare lecture
  14. September 1987 BICR Discussion and working
  15. September 1987 BICR Lecture and discussion
  16. September 1987 BICR Demonstrate methods
  17. September 1987 BICR Discussion and working
  18. September 1987 BICR Discussion with Director etc.
  19. September 1987 Prepare report
  20. September 1987 Prepare lecture
  21. September 1987 BICR Discussion in laboratories
  22. September 1987 BICR Lecture and discnssion
  23. September 1987 BICR Demonstrate in laboratories
  24. September 1987 BICR Demonstrate in laboratories
  25. September 1987 am BICR Discussions with Director and Staff
  26. September 1987 pm Meet UNIDO/UNDP Officers
  26. September 1987 Prepare report and sightseeing.
  27. September 1987 Complete report and sightseeing

- 28. September 1987 am Discussions with EICR Personnel  
pm Depart Beijing
- 29. September 1987 am Arrive Frankfurt → Vienna UNIDO de-briefing
- 30. September 1987 am De-briefing UNIDO HQ  
pm Depart Vienna → England  
24.00 hrs Arrive Home, Poole, Dorset, England

XVII APPENDIX 2.

SENIOR STAFF OF EICR

The following were present at many of the discussions

Mrs. SUN JING-YU	Director	Analyst
Mr. SUN SHI-MING	Associate Director	Analyst
ZHONG CHENG-XIAN	Former Director	Chemist
FAH BANG-LI	Chief Engineer	Chemist
LI JIA-BEI	Associate Chief Engineer	Analyst
LIEN CHENG-YI	Chief of Inorganic Laboratory	Chemist
WANG HUA-SHENG	Chief of Analytical Laboratory	Analyst
LI JIA-MAO		Chemist
LI CONG-KUN		Chemist
LI JIAN-GUO	Interpreter	Chemist
DANING-HUI	Interpreter	Electrical Engineer

Special Publication No 60

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## **Fine Chemicals for the Electronics Industry**

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The Proceedings of a Symposium organised by the  
Fine Chemicals and Medicinals Group of the Industrial Division  
of The Royal Society of Chemistry

University of Bath, 2nd-4th April 1986

Edited by  
**P. Bamfield**  
ICI PLC, Organics Division, Manchester

The Royal Society of Chemistry  
Burlington House, London W1V 0BN

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## Production of Fine Chemicals for the Electronics Industry

By L. P. Vergnano

3 Furze Hill Drive, Canford Cliffs, Poole,  
Dorset, BH14 8QL, England.

### INTRODUCTION:

This discussion includes the purification of single elements and any combination of elements in a high order of purity. It is mainly about the production of inorganic compounds.

One element may be combined with one or more elements to give a very wide variety of products. Frequently it is easy to remove certain impurities, but if they are closely related to any given Group in the Periodic Table or have similar properties, unusual methods may be used. Typically an organometallo compound may be used to produce a pure inorganic compound.

Elements with short half-lives are not discussed. They are shown in brackets when dealing with individual Groups in the Periodic Table.

### PURITY LEVELS:

Total metallic impurities is the sum of the elements detected by any suitable analytical technique and is expressed as tmi in parts per million (ppm).

It is essential to understand the magnitude of these figures. Most of the materials used in the preparation of Electronic Chemicals have their tmi in the order of 0.1-10 ppm. That is 1 part in 10,000,000 to 1 part in 100,000, which are very small quantities.

## *Production of Fine Chemicals for the Electronics Industry*

### HISTORICAL:

Purification can either be physical or chemical. There are many natural phenomena which occur, typically condensation of water which gives a pure material. The earliest applications were concerned with the extraction of metals. These arts were carried out without any theoretical knowledge, but often with skills that indicated long practice and a sound appreciation of materials.

Purification can be traced back to the earliest civilisation. The first known metal was probably gold where it was simply separated from river sands. Throughout the ages salt has been obtained by the evaporation of sea water. This is most likely the earliest form of purification by crystallisation.

From the earliest days there has been a requirement for pure materials as primary standards in analysis. There has been a progressive requirement for purer materials. After the First World War the analytical grades of materials were the best available. These grades were limited in number and quality. They did not include the wide range of elements and compounds which are available today.

The majority of the lanthanides were separated by fractional crystallisation and were not pure by modern standards. Salt available called 'didymium' which constituted a mixture of neodymium and praseodymium. Zirconium salts were always contaminated with hafnium, and niobium with tantalum and vice versa.

HEALTH AND SAFETY:

Frequently when dealing with unusual or rare compounds there is little known of their toxicity. Under these conditions it is essential to take adequate safety precautions when handling these materials. Equally precautions must be taken where there are known hazards. Request information from the suppliers of raw materials or from the local health and safety authority.

ANALYSIS:

The techniques applied many years ago are crude by today's standards. Nevertheless a competent analyst could obtain very accurate results with simple equipment.

The main tool used today for materials in process is optical emission spectroscopy for inorganic materials. There is a wide range of supporting methods for both inorganic and organic compounds.

APPARATUS AND TECHNIQUES:

In the early days the tools to use and the methods were very crude and laborious by today's standards. Filtration was through cloth and paper. One used simple crystallisation, fractional crystallisation through different solvents and sometimes simple or perhaps fractional distillation. Since the Second World War there have been many new techniques introduced. Ion-exchange resins have been made available, better solvents for extraction,

various forms of chromatography, sophisticated zone refining, selective decomposition of metal alkyls and many other methods.

Greater account has been taken of the environment with clean rooms and glove boxes. I believe the greatest aid of all has been the availability of modern plastics. Imagine handling hydrofluoric acid with only gutta-percha, platinum or very pure silver as the only materials of construction to obtain pure compounds.

Temperature control was very difficult in the regions above 900°C. These days sophisticated controls and furnace elements are available which allow easy control and a rapid rise in temperature.

Borosilicate glass is available, with vessels of up to 200 litres capacity having glass-to-glass seals. Imagine trying to prepare high purity materials using soda glass,orks and if lucky rubber bungs. On the larger scale there would be what would be regarded now as poor quality enamelled iron vessel: for volumes above 20 litres.

Today even with a very wide variety of reaction vessels, bearing in mind the low level of impurities required in the end product, it is essential to leach the container with a suitable solvent before use. This is particularly necessary when using plastics which frequently contain fillers and other leachable impurities.

PREPARATION AND PURIFICATION:

I can only give general guidance since there are a vast number of varying techniques which are learnt over the years. This is similar to having 'green fingers' in gardening when deciding on the best method to use. The best guide is to consider the individual elements in the same Group in the Periodic Table and it is most likely that those elements in the same Group will react in a similar manner. Advantage can be taken of any compounds which may slightly different reactions, in particular their solubilities.

Frequently advantage can be taken of the stability of one element in a different state of oxidation as opposed to the other in the same Group. Typically  $Fe^{3+}$  in a coordinated state is far less stable than  $Co^{3+}$ ; hence iron can be separated from cobalt.

As general guidance it is best to filter solutions at every stage possible during the purification. Always use scrupulously clean vessels at all stages. Care must be taken of the working area to ensure that impurities are not picked up from the environment. There is not much point in trying to remove iron, silicon and calcium if you are adjacent to a chalky sandy area.

Generally it is best to purify the individual element or one of its salts before combination. Always ensure that the purities of the reagents are compatible with the process. There is no point in using an iron-free material as reagent if the system

is already loaded with iron; it is an unnecessary expense. The converse is also true.

There are very few inorganic text books which give an adequate description of how to purify individual elements. Nevertheless it is always worthwhile to look at the standard works. If all else fails, look at the possibilities of organometallo or organometallic compounds since they are sometimes very easy to prepare and can be purified by distillation or crystallisation followed by decomposition by heat or a strong acid or base. Solubilities and melting and boiling points of the compound under purification should be examined with great care.

RAW MATERIALS:

These must always be selected with great care. The most expensive are not always the purest. Frequently a crude material can be the purest available. Typically potassium cyanide prepared immediately after the initial fusion is probably higher in KCN than in the tablet form. It may contain some free carbon, but that is easily removed. Where certain impurities are known to be difficult to remove from a given compound, always select a batch from the supplier which is low in the undesirable impurity. For example in the cases of hafnium and zirconium; niobium and tantalum; always look for one free of the other in each pair.

In the cases of precious metal and lanthanon compounds it is probably easier to purchase the pure element unless you are in the position for a high capital investment in plant.



Periodic table of the elements

18	New notation																VIIIA
	Previous IUPAC form																VIIIA
	CAS version																VIIIA
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	VIIIA
IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA	VIIIA	VIIIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 1.0079	He 4.00260	Li 6.941	Be 9.01218	B 10.81	C 12.011	N 14.0067	O 15.9994	F 18.9984	Ne 20.179	Na 22.9898	Mg 24.305	Al 26.9815	Si 28.0855	P 30.9738	S 32.06	Cl 35.453	Ar 39.948
K 39.0983	Ca 40.08	Sc 44.9559	Ti 47.88	V 50.9415	Cr 51.9956	Mn 54.9380	Fe 55.847	Co 58.9332	Ni 58.69	Cu 63.546	Zn 65.38	Ga 69.72	Ge 72.35	As 74.9216	Se 78.96	Br 79.904	Kr 83.80
Rb 85.4678	Sr 87.62	Y 88.9058	Zr 91.224	Nb 92.9064	Mo 95.94	Tc 98	Ru 101.07	Rh 102.905	Pd 106.42	Ag 107.868	Cd 112.41	In 114.82	Sn 118.71	Sb 121.75	Te 127.60	I 126.905	Xe 131.29
Cs 132.905	Ba 137.33	La 138.905	Hf 178.49	Ta 180.938	W 183.85	Re 186.207	Os 190.2	Ir 192.22	Pt 195.08	Au 196.967	Hg 200.59	Tl 204.383	Pb 207.2	Bi 208.980	Po (209)	At (210)	Rn (222)
Fr (223)	Ra 226.025	Ac 227.028	Unq (261)	Unp (262)	Unh (263)	Uns <sup>a</sup> (264)											

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.908	144.24	(145)	150.36	151.96	157.25	158.925	162.50	164.930	167.26	168.934	173.04	174.967
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.038	231.036	238.029	237.043	244	(243)	(244)	(247)	(251)	(252)	(257)	(258)	(259)	(260)

★ Lanthanide series  
▲ Actinide series

Note: Atomic masses shown here are the 1963 IUPAC values (maximum of six significant figures). a Symbols based on IUPAC systematic names.

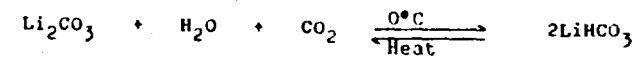
PERIODIC TABLE:

Experience has shown that it pays to look at the Periodic Table when attempting any method for separation of the elements. In the following text I look at each Group and discuss general methods of purification. Elements with short half-lives are shown in (). To avoid confusion the new proposed format of numbering the groups from 1-18 is used since it seems possible that this may be accepted by IUPAC. Organic, organometallo and organometallic compounds are shown separately.

GROUP 1: Hydrogen, lithium, sodium, potassium, rubidium, caesium, (francium), ammonia and its compounds.

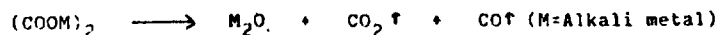
Hydrogen is generally purified by diffusion methods followed by adsorption on specially prepared palladium. The very pure gas is liberated by heating. Commercially pure hydrogen of a high standard is freely available.

Lithium is available as the carbonate and is easy to purify with the exception of calcium impurities. A soluble salt may be prepared and passed through a cation exchange resin in the H<sup>+</sup> form. Lithium carbonate may be dissolved in cold aqueous carbon dioxide. The solution is filtered and decomposed by heat:



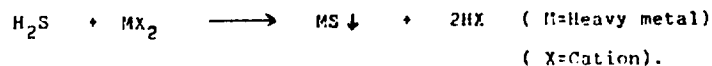
Sodium and potassium chlorides may be purified by filtering a strong aqueous solution into pure concentrated hydrochloric acid. The pure crystals are separated on a filter, washed and dried.

Rubidium and caesium are purified by fractional crystallisation of their mixed alkali halides, eg CsIBr<sub>2</sub> and CsICl<sub>2</sub>, where Cs=Rb. Examination of their solubilities will indicate the best method to remove other alkali metals. To produce the base the simplest method to use is the ignition of the almost insoluble oxalate:



Care must be taken to use a vessel for this ignition which is not attacked. If platinum is used carefully a product with tmi less than 5 ppm can be obtained.

If heavy metals are present in any of the alkali metal compounds they are best removed by treating an aqueous solution with hydrogen sulphide under neutral conditions:



Alternatively ammonium sulphide may be used.

Ammonia is easily purified by distillation of an aqueous solution and dissolving the gas in pure water for redistillation into a pure acid to give the pure salt. Alternatively a commercial ammonium salt may be recrystallised. Heavy metals are removed by the use of ammonium sulphide followed by filtration.

Advantage can sometimes be taken of the different boiling points of the alkali metals by carrying out a distillation under vacuum. Typically it is easier to remove all other metals from lithium. The problem is very often the vessel to carry out the process. High purity iron is a good material of construction. Boiling points:

Metal	Li	Na	K	Rb	Cs
B. Pt.	1336	883	762	696	670 °C at 760 mm Hg.

GROUP 2: Beryllium, magnesium, calcium, strontium, and (radium).

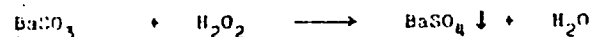
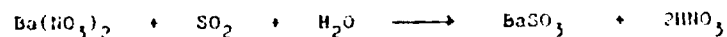
Care must be taken when handling beryllium, due to its high toxicity. It is best purified using its ability to produce basic salts. The basic acetate can be recrystallised from glacial acetic acid and sublimed to give a high purity salt. The acetate may be decomposed with a suitably pure acid to give a salt. Typically beryllium chloride may be prepared as follows:



Calcium, barium and strontium are usually contaminated with each other and magnesium. Careful selection of raw material will usually find a material low in magnesium which may be further reduced by recrystallisation of the nitrates. Use can usually be made of the varying solubilities of the sulphates:

Sulphate	Ba	Sr	Ca
Increasing solubility	→		

The best method is to saturate a solution of alkaline earth nitrate with sulphur dioxide and oxidise with hydrogen peroxide:



This process gives a finely divided barium sulphate which, although difficult to filter does give a good separation of barium from either strontium or calcium nitrate. In addition it will reduce the strontium in calcium nitrate.

Magnesium is best purified by sublimation under vacuum at 600 °C.

All compounds in Group 2 can be prepared with tmi less than 10 ppm.

GROUP 3 : Scandium, yttrium, lanthanum and (actinium).

The first three are found in association with the lanthanides and tend to be difficult to separate by conventional methods.

Scandium is usually extracted as the thiocyanate using diethyl or isopropyl ether. The ether solution is back extracted into water in the presence of excess ammonium thiocyanate. The pure scandium thiocyanate is decomposed with a pure acid of the desired ion :

$$\text{Sc(SCN)}_3 + 3\text{HX} \longrightarrow \text{ScX}_3 + 3\text{HSCN} \uparrow (\text{Very toxic}).$$

Yttrium is generally separated by solvent extraction or from the separation of the lanthanides which may be by solvent extraction or ion-exchange methods.

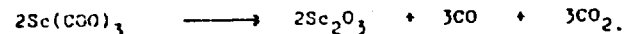
Lanthanum is usually obtained as a by-product from the lanthanide ion-exchange separation. It is usually free from other rare earths and most of the soluble salts can be recrystallised for purification.

All elements in Group 3 can be obtained with tmi less than 20 ppm. Further purification may be achieved by precipitation of their near insoluble oxalates by the addition of an aqueous pure solution of oxalic acid to a soluble salt :



Where X is the desired ion and Sc=Y=La.

The insoluble oxalate is washed with water, separated on a filter and ignited in a platinum crucible at 900°C :

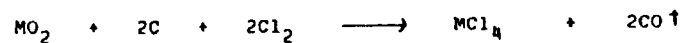


Where Sc=Y=La.

The tmi may be less than 5 ppm.

GROUP 4 : Titanium, zirconium and hafnium.

The tetrachlorides can all be prepared by heating the dioxides with carbon in a stream of chlorine :



Where M=Ti=Zr=Hf.

They will probably all contain arsenic, iron, tin and other heavy metals as contaminants. Titanium (IV) chloride may be purified by refluxing with copper powder followed by fractional distillation.

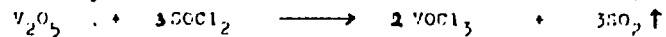
Hafnium and zirconium are difficult to separate but may be purified by solvent extraction, usually as the thiocyanate. Final purification may be effected by crystallisation of the oxydichlorides in the presence of a high concentration of hydrochloric acid.

GROUP 5 : Vanadium, niobium and tantalum.

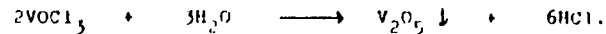
The high melting points of the metals make the preparation of the metals very difficult. The metals all tend to occlude oxygen, nitrogen and carbon. The salts will mostly contain other heavy metals.

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Use should be made of the various states of oxidation. In the case of vanadium, the oxytrichloride can be easily prepared by refluxing the pentoxide with thionyl chloride :



The oxytrichloride may be fractionated to give a very pure product which on hydrolysis with water will give a pure vanadium (V) oxide :

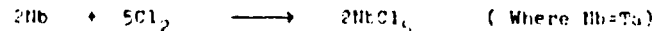


This may be further reduced with hydrazine in the presence of ammonium sulphate to give an alum which is easily crystallised and on ignition will give very pure vanadium (V) oxide with tmi less than 10 ppm.

Niobium is invariably associated with tantalum. The high melting points of the metals allow them to be heated in high vacuum to remove most metallic contaminants :

Melting points at 760 mm Hg : Nb 2468°C Ta 3025°C.

The (V) chlorides are easily formed by direct combination of the metal and chlorine :



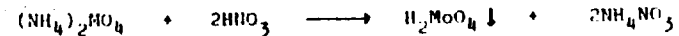
Sublimation can improve quality. The (V) chlorides are easily hydrolysed to give the (V) oxide :



GROUP 6 : Chromium, molybdenum and tungsten.

Chromium (VI) oxide may be recrystallised through concentrated nitric acid. The oxide being less soluble in nitric acid than water. This method will give a product with tmi less than 10 ppm.

The so-called ammonium molybdate of commerce may be purified by recrystallisation in excess of aqueous ammonia solution. The ammonium (VI) molybdate so formed is filtered and treated with pure nitric acid to give molybdic acid :



Subsequent washing will effect further purification to give a material with tmi less than 10 ppm.

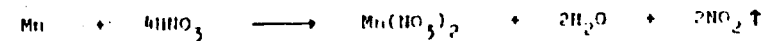
Sodium tungstate may be recrystallised from water and treated with nitric acid in a similar manner to ammonium molybdate; this will give tungsten (VI) oxide :



Subsequent washing will give a product which on drying may have tmi less than 10 ppm.

GROUP 7 : Manganese, (technetium) and rhenium.

Pure manganese metal may be obtained from the electrolysis of manganese sulphate in the presence of ammonium sulphate. Further purification may be effected by dissolution in nitric acid which in turn may be heated to give an oxide :



Although manganese (IV) oxide is indicated, the composition of the oxide varies with the temperature. Magnesium, which is a common impurity, may be removed by washing the oxide in dilute nitric acid in which it is almost insoluble. A product with tmi less than 15 ppm can be anticipated.

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Rhenium metal may be purified by heating rhenium metal in oxygen at 200-300°C. This will form the rhenium (VII) oxide :



which may be sublimed at 250°C to a material with tmi less than 10 ppm.

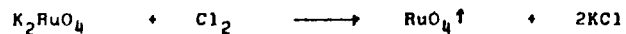
GROUP 8 : Iron, ruthenium and osmium.

The purest iron available is obtained from the carbonyl process. The main contaminants are manganese with traces of other heavy metals. Dissolution in hydrochloric acid gives the iron (II) chloride:



If this solution is treated under reducing conditions or in an inert atmosphere with ammonium sulphide in a near neutral solution, the insoluble heavy metal impurities may be removed by filtration. This will give a very pure solution which may be used in the preparation of other iron compounds.

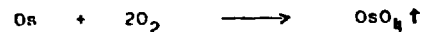
Ruthenium may be purified by passing chlorine through an solution of a ruthenate giving the highly volatile ruthenium (VIII) oxide :



This oxide may be distilled to a product with tmi of less than 10 ppm. Care must be taken to avoid contact with any organic materials including plastics with which it can explode.

Osmium metal is easily purified by burning in pure dry oxygen to give the highly volatile osmium (VIII) oxide :

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The oxide is distilled to give a product with tmi less than 5 ppm. This is equally a strong oxidising agent but not so vigorous as ruthenium (VIII) oxide. Nevertheless care must be to avoid contact with reducing agents.

GROUP 9 : Cobalt, rhodium and iridium.

Cobalt of commerce invariably contains nickel, iron and manganese. These impurities may be removed by the formation of  $\text{Co}^{3+}$  ammine complexes. The complex is washed with a suitable acid which will remove the impurities since they do not form a corresponding complex.

Rhodium (III) chloride is prepared by passing chlorine over heated rhodium metal :

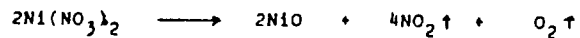
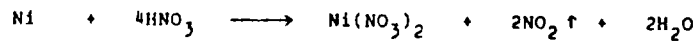


This may be purified by resublimation to give a material with tmi less than 10 ppm.

Ammonium chloroiridate may be treated with aqua regia after washing with various solvents to give a substantially pure chloroiridic acid.

GROUP 10 : Nickel, palladium and platinum.

Nickel is usually obtained in a pure state from the carbonyl process. Further purification may be carried out by dissolution in nitric acid followed by the recrystallisation from dilute nitric acid:

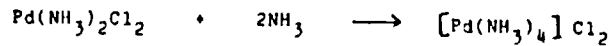


A product with tmi less than 10 ppm can be anticipated.

Ammine compounds of palladium are easily prepared by treating chloropalladous acid with aqueous ammonia :



The diammine which is precipitated may be washed in further hydrochloric acid, washed free of acid with water and dissolved in an excess of ammonia solution :



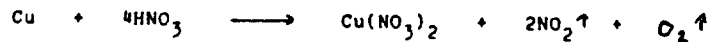
The tetramminepalladium(II) chloride may be crystallised and dried to give tmi less than 10 ppm.

A similar route may be used to prepare a pure tetrammineplatinum(II) chloride.

GROUP 11 : Copper, silver and gold.

All the metals may be purified by electrolysis. Nevertheless it is best to carry out some initial chemical processing.

Electrolytic copper may be dissolved in nitric acid :



The nitrate so formed may be filtered cold, the solution evaporated and precipitated with pure concentrated nitric acid. After the crystals are separated they will contain tmi less than 5 ppm, if

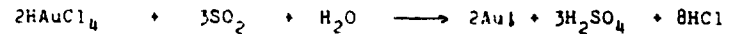
a careful choice of raw materials is made.

Silver chloride is prepared by the addition of pure hydrochloric acid to an aqueous solution of pure silver nitrate :



The chloride may be dissolved in an excess of aqueous ammonia solution. The ammine complex is explosive if dried. Great care must be taken to keep wet. The solution is filtered and heated with dextrose in the presence of sodium hydroxide to give silver metal. This may be washed with water giving material with tmi of less than 5 ppm.

Chloroauric acid is prepared by the dissolution of gold in aqua regia and boiling with an excess of hydrochloric acid. The solution is cooled and filtered to remove any insoluble silver chloride. Sulphur dioxide is passed through the solution to precipitate gold :



Subsequent washing with water will give a product with tmi less than 5 ppm.

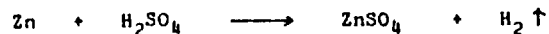
GROUP 12 : Zinc, cadmium and mercury.

These three elements may be distilled to purify, although cross contamination can be a problem.

Cadmium compounds form soluble complexes with ammonia solution.

Filtration after treatment with ammonium sulphide will remove other heavy metals. Sufficient acid is added to give a partial precipitation followed by filtration. This is followed by the addition of further ammonium sulphide to give a faint precipitate and once more filtered. Gentle ignition will break down the complex to give a pure base with tmi less than 15 ppm.

Electrolytic zinc is relatively pure. Further purification may be effected by dissolution in sulphuric acid :



An aqueous solution of zinc sulphate is passed through a specially prepared alumina column which removes heavy metals. Other impurities may be removed by treating a near neutral solution with hydrogen sulphide followed by filtration. The pure solution is electrolysed using platinum electrodes. Metal with tmi of less than 10 ppm may be obtained.

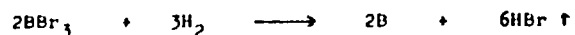
Mercury is purified by recrystallisation of the nitrate followed by heating to decompose in two stages



Final distillation under reduced pressure will a product with tmi less than 1 ppm.

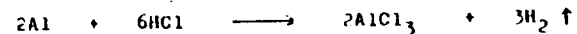
GROUP 13 : Boron, aluminium, gallium, indium and thallium.

Very pure boron can be obtained by distillation of boron tribromide followed by reduction under hydrogen :



Zone refining under hydrogen can give boron with tmi of less than 5 ppm.

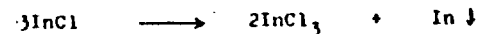
Commercial aluminium usually has a high iron content. This can be removed by dissolution in hydrochloric acid :



The solution is then passed through an anion-exchange resin in the  $\text{Cl}^-$  form where the iron is removed as the  $(\text{FeCl}_4)^-$  ion. The solution is filtered and evaporated and the hexahydrate is obtained by the addition of pure concentrated hydrochloric acid. After separation and washing with hydrochloric acid the tmi are less than 5 ppm.

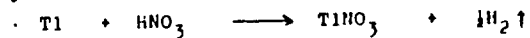
Gallium usually contains aluminium, copper and mercury as the major impurities. Mercury may be removed by heating to a high temperature in a stream of hydrogen since the boiling point of gallium at 760 mm Hg is  $2064^\circ\text{C}$ . Further purification can be effected by recrystallisation under weak hydrochloric acid. Since the melting point is  $29.8^\circ\text{C}$  this is very simple, but does require expertise in separation.

All indium halides may be prepared by the direct combination of the elements. Disproportionation of the lower halides in different solvents can effect good purification. Typically indium(I)chloride can give indium(III)chloride and after washing indium metal with tmi less than 1 ppm :

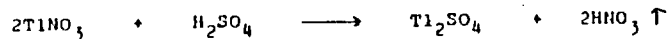


A further purification is made by zone refining.

Thallium usually contains a wide variety of impurities, in particular lead, cadmium, nickel, zinc and palladium. The best initial purification is dissolution of the metal in nitric acid:



Advantage should be taken in the solubility of thallium(I) nitrate in hot and cold water, 4g/100 ml at 0°C and 593.9/100 ml at 100°C. Recrystallisation is an obvious choice. This is followed by decomposition with sulphuric acid:

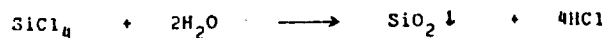


Electrolysis of the sulphate will give a thallium metal with tmi less than 5 ppm.

GROUP 14: Carbon, silicon, germanium, tin and lead.

The majority of the hydrocarbons can be purified by distillation. These may be burnt in a deficiency of oxygen to give pure carbon.

There has been more work carried out on silicon than any other element in recent years. Purification of silicon(IV)chloride is the best initial step, usually by boiling under reflux with copper powder, which forms an arsenide with the arsenic which is generally present. This is followed by fractional distillation. Hydrolysis of the chloride followed by boiling gives silicon(IV)oxide:



The insoluble oxide may be further washed to purify. Elemental silicon may be obtained by heating the chloride with carbon at a high temperature. The final purification is by zone refining.

Tin metal may be heated in a stream of chlorine to give tin(IV)chloride:

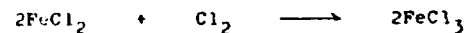
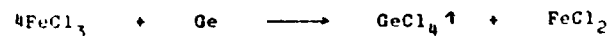


The chloride is fractionally distilled and treated with an aqueous solution of ammonium chloride to give ammonium hexachlorostannate:

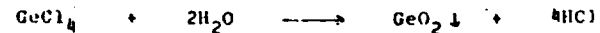


which may be purified by recrystallisation followed by electrolysis to give a pure metal with tmi less than 5 ppm

Germanium is available in many crude forms and is frequently found in the residues from zinc smelting and flue dusts from coal burning. It is best treated by fusion under reducing conditions with iron powder where an alloy is formed. The alloy is ground and treated with chlorine in acid solution to give iron(III)chloride which acts as a chlorine carrier and in turn is reduced to iron(II) chloride giving germanium(IV) chloride



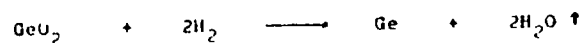
The process is carried in the presence of aqueous hydrochloric acid and the germanium(IV)chloride is distilled at 84°C which may be fractionally distilled in the presence of copper foil. Hydrolysis with water gives germanium(IV)oxide:



which may well have tmi less than 5 ppm. The oxide may be



reduced under hydrogen to give germanium metal :

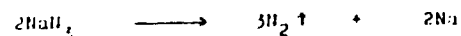


The metal is then zone refined to have less than 1 ppm metallic impurities.

Lead(II)acetate is the simplest lead salt to purify although calcium may be difficult to remove. Electrolysis can give a metal with tmi less than 5 ppm. Alternatively lead(IV)acetate may be crystallised using glacial acetic acid as a solvent.

GROUP 15 : Nitrogen, phosphorus, arsenic, antimony and bismuth.

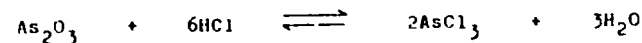
Nitrogen can be obtained commercially in a high order of purity since it is the product from the fractional distillation of air. Extremely pure nitrogen may be obtained by the careful decomposition of sodium azide by heating. This material is explosive and suitable precautions must be taken :



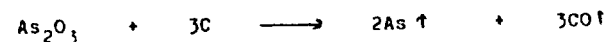
White phosphorus may be washed with cool dilute sodium hydroxide followed by washing with water. A further wash with cool dilute sulphuric acid is followed by further washing with water. This process must be carried out with good extraction in case the toxic phosphine is liberated. Steam distillation will give a material with tmi less than 5 ppm. Alternatively the phosphorus chlorides may be fractionated.

Arsenic(III)oxide is dissolved in concentrated hydrochloric

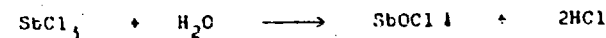
acid by heating under reflux followed by good filtration and hydrolysis with a large excess of water. The reaction is reversible and favours the formation of arsenic(III)chloride in the presence of high concentrations of hydrochloric acid :



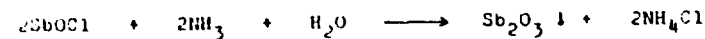
Pure elemental arsenic may be obtained by reduction with carbon and sublimation under high vacuum :



Antimony(III)chloride may be purified by fractional distillation, the head fraction containing the major impurity, namely arsenic. Subsequent hydrolysis will give antimony(III)oxychloride :

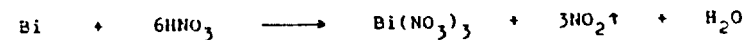


This is washed with water followed by boiling with aqueous ammonia solution to give antimony(III)oxide :



After washing free of chloride and drying the product will have tmi less than 10 ppm.

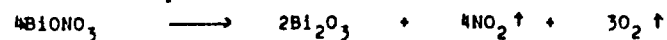
Bismuth metal of commerce is relatively pure. Further purification may be effected by dissolution in strong nitric acid to form bismuth(III)nitrate :



The nitrate may be recrystallised from nitric acid followed by hydrolysis to give bismuth(III)oxynitrate :



which may be washed with very weak nitric acid, separated and subsequently heated to give bismuth(III)oxide :



The material should have tmi less than 5 ppm.

GROUP 16 : Oxygen, sulphur, selenium, tellurium and (polonium).

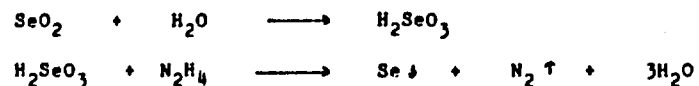
Commercial oxygen is obtainable usually in a very high order of purity since it is a product from the fractional distillation of air. Pure oxygen may also be prepared by the catalytic decomposition of hydrogen peroxide.

Sulphur is purified by the dissolution in carbon disulphide followed by filtration and recrystallisation. Alternatively slow sublimation can give very good results. In either case the tmi should be less than 5 ppm.

Elemental selenium is burnt in oxygen and the vapour may be passed through fuming nitric acid to give selenium(VI)oxide :

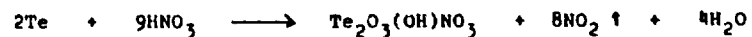


This may be resublimed to give a product with tmi less than 1 ppm. Alternatively the oxide may be dissolved in water to form selenous acid and reduced with hydrazine hydrate to give pure elemental selenium :

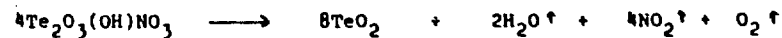


Tellurium of commerce is usually contaminated with selenium and

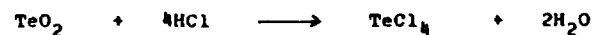
sulphur. It is dissolved in nitric acid at a low temperature to give a basic nitrate :



The nitrate is purified by recrystallisation and ignited to give tellurium(IV)oxide :



This may be dissolved in hydrochloric acid to give a solution of tellurium(VI)chloride :



which after filtration is reduced with hydrazine hydrate to give elemental tellurium :



which, after washing and drying should have tmi less than 5 ppm.

GROUP 17 : Fluorine, chlorine, bromine, iodine and (astatine).

Free fluorine is rarely required unless for direct combination. Ammonium hydrogen fluoride may be recrystallised from water and heated gently to give a relatively pure hydrofluoric acid :



Alternatively 60% hydrofluoric acid may be treated with lead carbonate which forms lead chlorofluoride and chloride. Both are insoluble and may be removed by filtration. Treatment with a solution of barium hydroxide followed by filtration will remove the sulphuric acid as insoluble barium sulphate. The acid is adjusted to about 40% and distilled in a platinum or a pure silver apparatus to tmi less than 20 ppm.

Commercial chlorine is best condensed at  $-34.6^{\circ}\text{C}$  in a bath of solid carbon dioxide and acetone. This may be repeatedly vaporised and condensed while non-condensable gases such as nitrogen and oxygen are removed by distilling under high vacuum using liquid nitrogen as a coolant. Pure hydrochloric acid is obtained by repeatedly distilling the 20.24% constant boiling mixture which boils at  $110^{\circ}\text{C}$ .

Bromine is easily purified by a distillation at  $58.78^{\circ}\text{C}$  over potassium bromide, which removes the main volatile impurity which is chlorine. Bromine may also be dried by distillation over phosphorus(V)oxide.

Iodine is easily purified by very slow sublimation in a glass casserole. If chlorine or bromine are present the crude material should be mixed with potassium iodide. Iodine can also be purified by steam distillation.

GROUP 18 : Helium, neon, argon, krypton, xenon and (radon).

All these gases are available in a high order of purity and are mainly obtained from the fractional distillation of air.

LANTHANIDES : Cerium, praseodymium, neodymium, samarium europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and (promethium).

Lanthanum has already been discussed under Group 3.

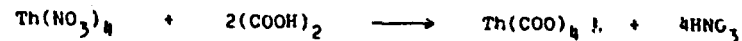
Cerium is easily separated since it is unusual in the lanthanide series in exhibiting a stable  $4+$  oxidation state. Advantage is taken of this when separating from the other lanthanides.

The remainder of the series may only be separated by a combined system of ion-exchange resins using specific buffers for the elution. This is supplemented by solvent extraction. Advantage is taken of any variation in oxidation states. All the lanthanides have the  $3+$ , but others such as europium, samarium and ytterbium exhibit the  $2+$  state. Where insoluble salts such as europium(II) sulphate exist they can be used as method of separation.

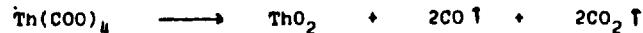
All the metals may be prepared by heating the oxide or fluoride to high temperatures with either calcium or lanthanum metal under high vacuum. Frequently sublimation is used as a method of purification. The majority of the metals and compounds can be obtained with tmi less than 20 ppm or better.

ACTINIDES : Thorium and uranium (the remainder have short half-lives and are rarely, if ever, used in the Electronics Industry).

Thorium is usually available as the (IV) nitrate and is usually quite pure. Further purification may be effected by dissolution in weak nitric acid and recrystallising. A pure solution of oxalic acid is added to a filtered aqueous solution of the nitrate to precipitate the almost insoluble thorium(IV)oxalate:

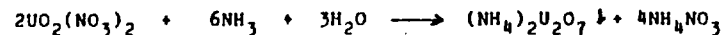


This is followed by washing with weak nitric acid and water. After separation the material is ignited in a platinum dish at 800°C :

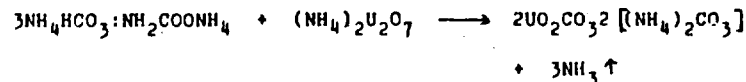


The thorium(IV)oxide will have tmi less than 10 ppm.

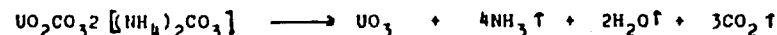
Uranium is usually available as uranyl nitrate and is generally quite pure. Recrystallisation will improve the quality. Further purification is carried out by treating an aqueous solution of this nitrate with aqueous ammonia to form ammonium uranate(IV) :



This is washed thoroughly with water and dissolved in excess ammonium carbonate solution to give ammonium dioxotricarbonato-uranate(IV) :



This salt may be recrystallised from water, separated and ignited at 200°C to give uranium(VI)oxide :



Heating to higher temperatures tends to give lower oxides.

The anticipated impurities should be less than 10 ppm.

#### ORGANIC MATERIALS :

There is a wide variety of high purity solvents used for cleaning and the preparation of electronic devices. All the standard

Organic methods of purification are used. Many methods such as chromatography which at one time would not be considered a practical production method are now used to produce quite large quantities of materials. Many specialised methods have been developed for production. Organic chemicals for the Electronics Industry is a fast growing business.

#### ORGANOMETALLO MATERIALS :

Alkyl and aryl derivatives of many elements are purified as intermediates to prepare elements and compounds with a very high order of purity. Frequently these are compounds of mercury and lead which require very specialised techniques and usually costly apparatus due to their high toxicity. Nevertheless they play an important part in the Electronics Industry.

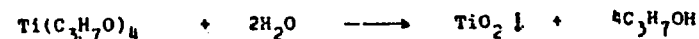
The following indicates some of the materials that are available and their applications :

Tetraethoxy silicate, bp 165-166°C, may be fractionated in glass to give a very pure material which on hydrolysis in water in the presence of hydrochloric acid or ammonia solution will, after boiling give an easily manageable silicon dioxide :



After washing and ignition the tmi should be less than 5 ppm.

Tetrakispropoxytitanium, bp 58°C/1 mm Hg is fractionated in glass under vacuum and treated in a similar manner to silicon alkoxides to give titanium dioxide :

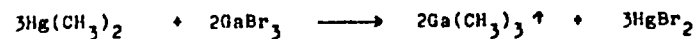


After washing and ignition the tmi should be less than 5 ppm.

ORGANOMETALLIC MATERIALS :

Orignard reagents are frequently used in the preparation of organometallic compounds. There is a wide variety alkyl complexes that are used for metal-organic vapour phase deposition (MOCVD) which gives epitaxial layers. They are used by passing a carrier gas through the liquid or heated solid organometallic compound..

Typically trimethyl gallium may be prepared as follows :



Trimethyl gallium is separated by distillation and for MOCVD.

Most of these compounds are highly toxic and frequently pyrophoric. Various compounds of aluminium, cadmium, indium, tin, selenium, tellurium, tin and zinc are used. In addition hydrides are frequently for epitaxial growth layers.

CONCLUSION :

I have given a brief outline showing some of the methods used in the manufacture of high purity chemicals and elements or a base from which other compounds may be prepared. Do not accept that these are the only only methods of purification for a given raw material. It is wiser before starting a process to examine all the impurities in the raw material and tailor make the process. Do not worry if the route is unorthodox; it may work.