Chemistry of Superconducting Radio Frequency Cavities

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Outline of the talk

- Chemistry of Niobium
- Processes that involve chemicals/chemistry
- Chemistry of processes
- Chemistry in process control
- Treatment and disposal

Chemistry of Niobium (Colombium)

Atomic Number 41

Atomic Weight 92.91 g/mole

Electronic configuration – [Kr] $4d^4$ $5s^1$

Group 5 of periodic table (V, Nb, Ta)

Oxidation states 5, 4, 3, 2, 1, -1, -3

Extremly sensitive with H, O, C,N,S & halogens

Fluorides, Chlorides, Bromides, Iodides, oxides, sulfides, nitride having various oxidation states.

Oxides:

Nb_2O_5, NbO_2, Nb_2O_3, NbO with oxidation state of 5, 4,3 and 2 respectively.

Halides:

NbX_5 and NbX_4 (X= F, Cl)

Both are hydrolyzed to give oxides and oxy halides such as $NbOCl_3$.

Anionic halide compounds are will known due to lewis acidity (electron acceptor) of penta halides.

$[NbF_7]^{2-}$, $[NbCl_6]^-$ are some examples.

Processes that involve chemistry

- Buffered Chemical Polishing (as pre-weld etch of formed half cells before EB welding)
- Electropolishing (Cavity processing)
- Process control
- Ultrapure water for rinsing
- Treatment and disposal of solutions

Buffered Chemical Polishing (BCP) for Pre-weld etch

- During fabrication the outermost layer of niobium is damaged and contaminated by foreign materials and must be removed.

- Chemical etching has been found to be an appropriate method for this purpose. Buffered chemical polishing and Electropolishing are two major approaches for this purpose.

- BCP treatment is used as a pre-weld etch in preparing the niobium half cells for EB welding at RRCAT.

Procedure adopted for pre-weld etch of half cells

1. Swipe cleaning with iso propanol

2. Ultrasonic cleaning in detergent to remove oil ,grease and dust particles.

3. Washing with DM water

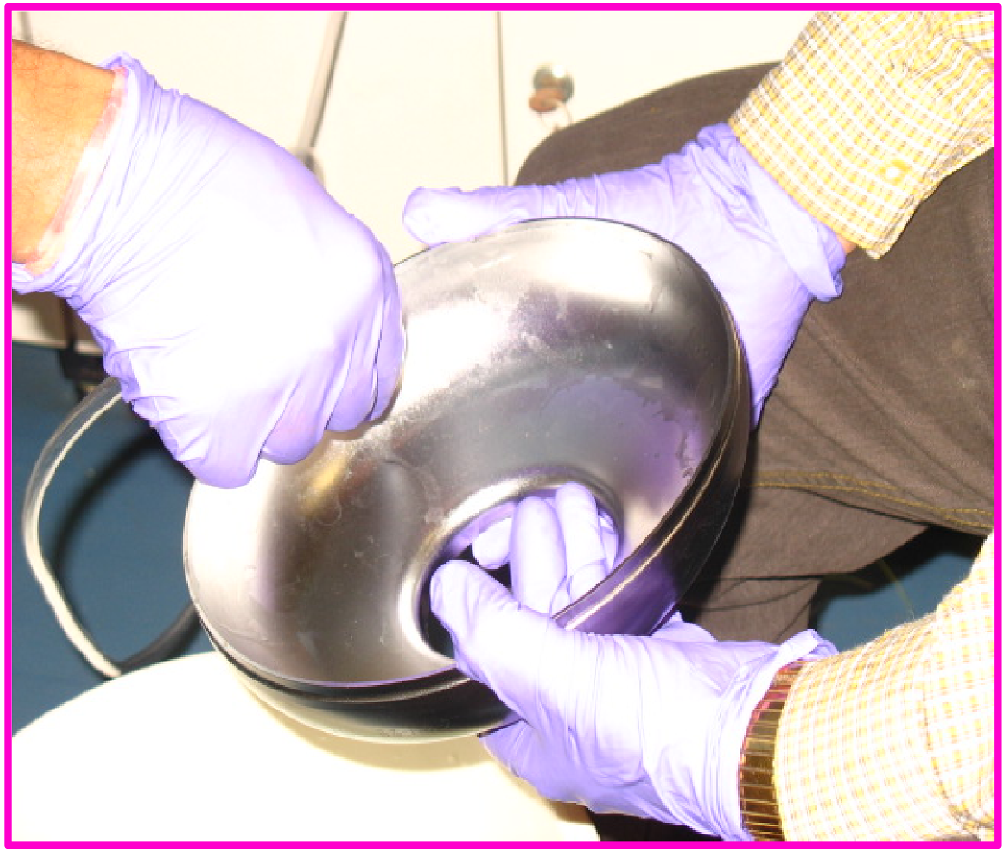
4. Immersion in buffered chemical polishing solution

    Time 20 minutes

    Temperature 15 to 18°C

5. Wash with DM water and ultrasonic cleaning with DM water

5. 6. Dry with nitrogen



BCP of Niobium half cells 1.3 GHz

- BCP uses a mixture of three acids, hydrofluoric acid, nitric acid and orthophosphoric acid in the ratio 1:1:1 or 1:1:2.

- Acid temperature is kept below 20ºC

- Etch rate approximately 1 micron per minute

- 15 to 20 microns removed after fabrication of half cells.

- Niobium concentration in the bath should be kept below 15 g/l

- Nitric acid reacts with Nb to form di-Niobium pentoxide (Nb_2O_5)
- Hydrofluoric acid reacts with this pent-oxide to form water soluble NbF_5.
- Ortho phosphoric acid serves as a buffer helping in keeping constant the reaction rate. This depends on the temperature and concentration of Nb in solution.
- Nitrogen dioxide, Nitric oxide were evolved during the reaction.
- Emission of nitric acid and hydrofluoric acid also takes place.

(Ref: Facility for Chemical Polishing of Superconducting Niobium RF cavities, C.Boffo et al.,)

$6\ Nb + 10\ HNO_3 \dashrightarrow Nb_2O_5 + 10\ NO + 5H_2O$

$Nb_2O_5 + 10\ HF \dashrightarrow 2\ NbF_5 + 5\ H_2O$

Acid mix is very corrosive and cause severe burns if gets to human skin.

Handling the acid requires full body protection chemically resistant suite, mask, gloves, and boots.

Storing of this solution is also difficult and it will be better if the quantity required for one time is prepared.

Material compatible with these acids PVDF or PTFE.

Double tank set up

Second Rinse

Ultrasonic cleaning

Packing under
nitrogen atmosphere

Pre-weld etching of 650 MHz
Niobium half cells in BCP solution

Behaviour of HNO_3 with Niobium

Ref: A. Aspart, C.Z. Antoine
DSM / DAPNIA / SACM, BP 702

Nitrate ions from nitric acid oxidizes Niobium to Nb_2O_5 (+5 oxidation state)

$$6\ Nb + 10\ HNO_3 \rightarrow 3Nb_2O_5 + 10\ NO\uparrow + 5\ H_2O$$

Water plays an important role in the chemical behaviour of solutions.

Nb_2O_5 created in presence of water leads to diverse form of niobic acids

$H_4Nb_4O_{12}$ or 2 Nb_2O_5 .$2H_2O$ (di niobic)

$H_7Nb_3O_{11}$ or 3 Nb_2O_5 .$7H_2O$ (tri niobic)

$H_7Nb_5O_{16}$ or5Nb_2O_5 .$7H_2O$ (penta niobic)

Colourless NO produced is converted to reddish brown NO_2 or N_2O_4

Behaviour of HF with Niobium

Ref: A. Aspart, C.Z. Antoine
DSM / DAPNIA / SACM, BP 702

When phosphoric or sulphuric acid is not introduced, Nb_2O_5 is readily transformed by HF into fluoride and oxofluoride acidic species depending on the concentration of HF.

In the absence of nitric acid, thin Nb_2O_5 is readily dissolved by HF in a short while and then the reaction stops.

$$Nb_2O_5 + 14\ HF \Leftrightarrow 2\ H_6NbO_2F_7 + H_2O$$

$$Nb_2O_5 + 12\ HF \Leftrightarrow 2\ HNbF_6 + 5\ H_2O$$

$$Nb_2O_5 + 10\ HF \Leftrightarrow 2\ NbF_5 + 5\ H_2O$$

$$Nb_2O_5 + 10\ HF \Leftrightarrow 2\ H_2NbOF_5 + 3\ H_2O$$

$$HNbF_6 + HF \Leftrightarrow H_2NbF_7$$

In the absence of HF, the presence of passive layer of Nb_2O_5 prevents the dissolution of Nb.

Behaviour of H_2SO_4 with Niobium

Ref: A. Aspart, C.Z. Antoine
DSM / DAPNIA / SACM, BP 702

Sulfuric acid behaves as a complexing agent with Niobium to form oxy-sulfate compounds.

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$$
$$Nb_2O_5 + n\, H_2SO_4 \rightarrow Nb_2O_{5-n}(SO_4)_n + n\, H_2O$$
$$2NbF_5 + (5-n)H_2SO_4 + nH_2O \rightarrow Nb_2O_n(SO_4)_{5-n} + 10\, HF$$

At high concentrations, the elevated viscosity of the sulfuric solution contributes to the synthesis of a passive layer.

Moreover, as this acid is highly hygroscopic when concentrated, the hydrolysis of HF and HNO_3 by water is strongly reduced, and the quantity of complexing F- and oxidizing NO_3^- anions free in solution is decreased.

Ref: A. Aspart, C.Z. Antoine
DSM / DAPNIA / SACM, BP 702

The reverse reactions (to the left side) equilibriums are consequently favoured:

$$HF + H_2O \rightarrow H_3O^+ + F^-$$

$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$$

This phenomenon induces the decreasing of the niobium dissolution rates.

Others reactions also exist between NbF_5 andsulfuric acid, considered as hydrated sulfur trioxide (SO_3, H_2O). The following equations lead to Nb(V) fluorosulfate or oxysulfate, plus pyrosulfurylfluoride

$$NbF_5 + 2\,(SO_3, H_2O) \Leftrightarrow NbF_3(SO_3F)_2, 2\,H_2O$$

$$2\,NbF_5 + 14\,SO_3 \Leftrightarrow Nb_2O(SO_4)_4 + 5\,S_2O_5F_2$$

(Electro) Chemistry of Electropolishing

[Ref: Landolt]

Electropolishing: Improvement of the surface finish of a metal by making it anodic in a suitable solution.

Ideal polishing process can be distinguished as

Smoothing by elimination of large scale irregularities.
(anodic levelling or macrosmoothing)

Brightening by removal of smaller irregularities.
(anodic brightening or microsmoothing)

Macro (anodic) Smoothing: Elimination of surface roughness of height greater than 1 micron.

The formation of relatively thick viscous layer of reaction products around the anode controls the smoothing action.

Presence of viscous layer is intimately associated with polishing.

The composition of viscous layer is difficult to determine because of its complex chemical nature and difficulties in sampling.

Smoothing during electrpolishing can be accounted for qualitatively by the differences in concentration gradient in the viscous layer over peaks and valleys.

At the peaks the layer is thin, higher concentration gradient while in the valleys the layer is thicker and concentration gradient is lower.

Concentration of current lines on peaks of a surface profile thus leading to a locally higher dissolution rate.

Micro Smoothing (brightening): Elimination of surface roughness of height less than 1 micron.

Microsmoothing results from the suppression of surface defects and crystallographic orientation on the dissolution process.

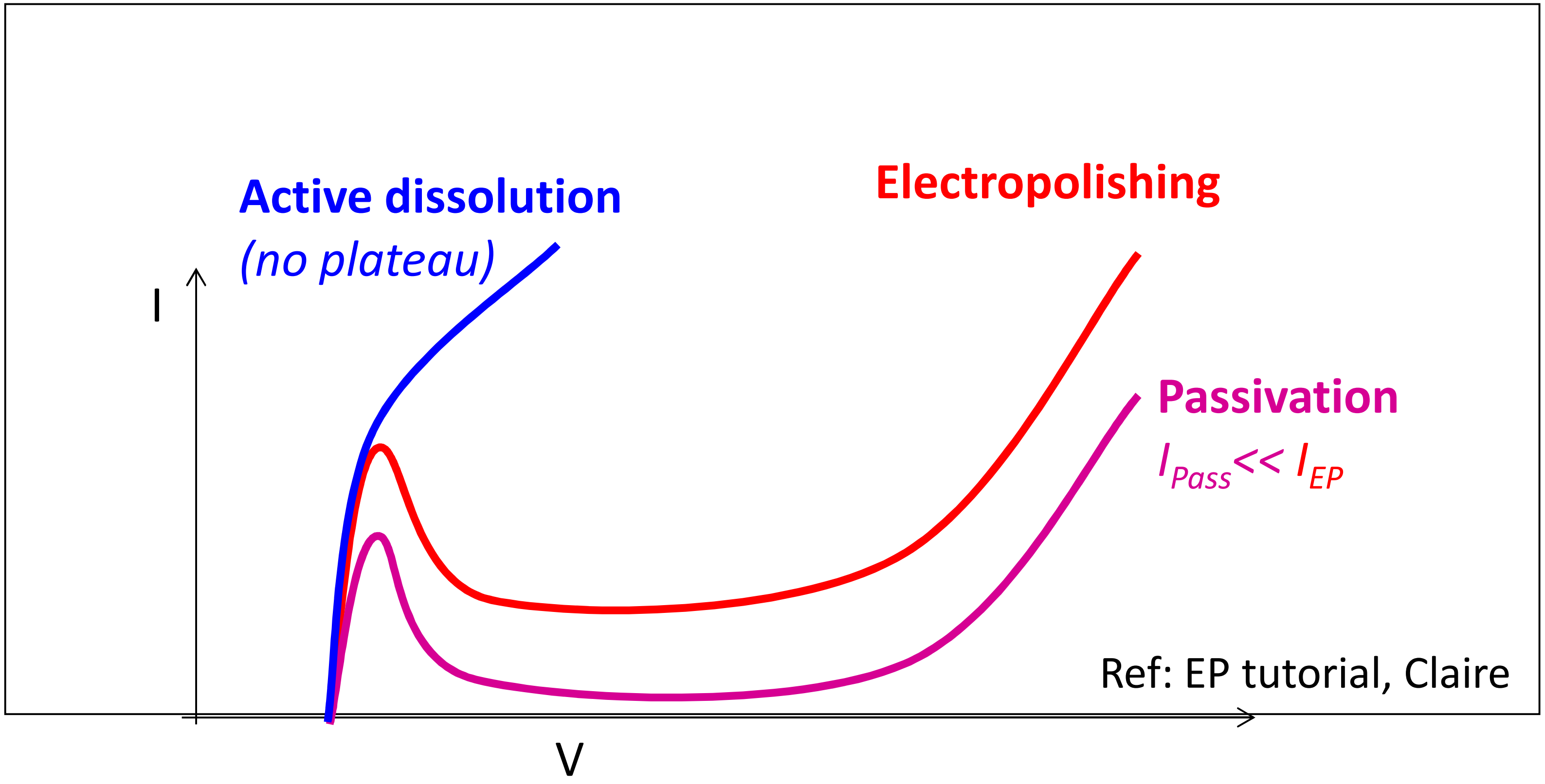
In practice, it is possible to achieve microsmoothing without macrosmoothing and vice versa.

Many of the observations on the polishing process can be interpreted readily in terms of classical electrochemistry.

These processes are related to the well-known anodic phenomena of concentration over potential and passivity.

Conditions of the polishing process are more restricted than those for anodic process.

It is necessary to consider polishing as a special case.



Ref: EP tutorial, Claire

Current (I) Versus Voltage (V) curves for different processes

- Active dissolution : the metal is soluble
- Passivation: an **insulating** oxide or compound builds up on the surface *builds up in dilute acid solutions*
- EP : high resistivity layer formed on the surface, but it is more conducting (ions) compared to passivation *builds up in concentrated solutions*

Three possible transport mechanisms have been proposed in the literature for electropolishing

(i) Salt precipitation mechanism

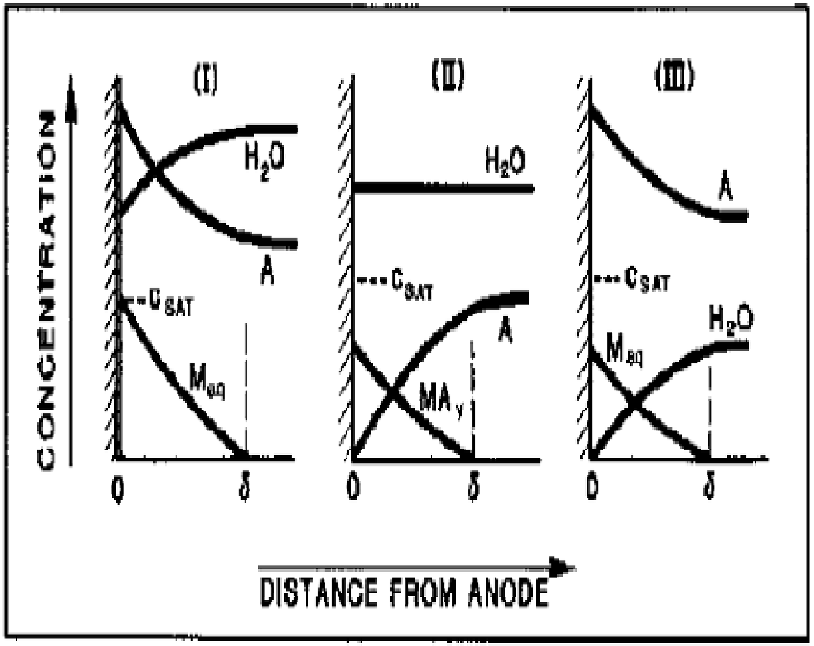
(ii) Rate limiting diffusion of acceptor anions which are consumed at the anode by the formation of complexes and

(iii) Rate limiting diffusion of water from the bulk to the anode where it is consumed by formation of hydrated metal ions

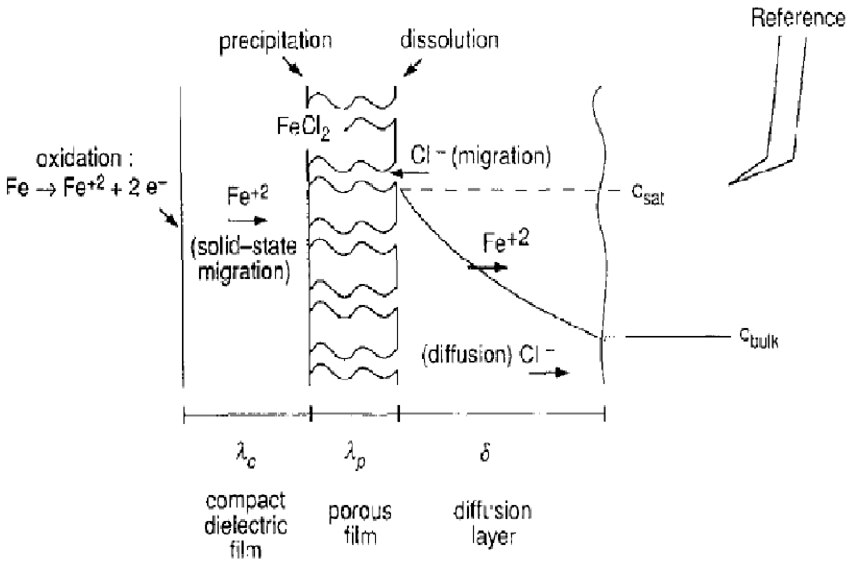
[Ref: Landolt]

- Microlevelling : only possible under transport control
- At the limiting current the current distribution is governed solely by mass transport.

Transport limiting species : 3 cases



[Landolt]



[Matloz M]

- Mixture of sulfuric (95 – 98%) acid and hydrofluoric acid (48%) , H_2SO_4 : HF = 9 : 1
- 2.76 moles of HF and 16.56 moles of H_2SO_4
- Acids must be cooled before mixing to minimize heat generation.
- Addition of sulfuric acid to HF is preferred along with cooling and constant stirring. Special care to be taken if added in reverse order

$$2\,Nb + 5\,SO_4^{2-} \text{ ------> } Nb_2O_5 + 10H^+ + 5SO_4^{2-} + 10e^-$$

$$Nb_2O_5 + 6HF \text{ ------> } H_2NbOF_5 + NbO_2F0.5H_2O + 1.5\,H_2O$$

$$NbO_2F0.5H_2O + 4HF \text{ ------> } H_2NbOF_5 + 1.5\,H_2O$$

(Ref: N. Steinhau-Kuhl etal)

Many studies have been performed by the SRF community to understand the effect of polishing parameters on cavity performance, as well as the mechanism and quality control of the process.

Water concentration increase provoked a premature deterioration of the niobium samples surface.

High [HF]/[H_2O] ratio seems desirable to achieve efficient electropolishing with a long life time of the mixture

Electrochemical Impedance Spectroscopy results are consistent with the compact salt film mechanism for niobium electropolishing (EP).

Rotating disc electrode studies on limiting current density demonstrates a clear dependence on fluorine diffusive mass transport.

In a fresh EP solution, diffusion coefficient of fluoride ion (D_{F^-}) is high and a compact film is formed at the surface of niobium.

With the aging bath, D_{F^-} decreases thereby decreasing the removal rate of oxide layer and making it thicker.

The concentration of hydrofluoric acid in the electropolishing solution will be reduced due to (i) continuous vaporization of the acid in the mixture during recirculation and (ii) formation of complexes with niobium dissolved from the cavity during the electropolishing process.

Amount of dissolved niobium is the retained parameter for changing electrolytes. Niobium concentrations up to 9 grams per litre are used without performance deterioration

Periodic oscillations of current and voltage may occur in a cell before polishing conditions are established.

They are due to periodic growth and destruction of a thin oxide film on the surface of the anode.

The film follows the contours of the surface and is attacked uniformly by the electrolyte. This causes brightening

(Analytical)Chemistry of Process Control

1. Analysis of Fluoride ions in EP solution
2. Analysis of Sulphate in EP solution
3. Analysis of Niobium in EP solution
4. Analysis of ultrapure water
5. Analysis of treated and untreated EP acid and waste water

Difficulties in process control of EP solution

- Highly corrosive liquid, causes damage to instrument, glass wares etc
- Complex compound formation, difficulty in obtaining reliable and accurate results.
- Hydrolysis after dilution, values change with storing time after sample preparation in water and analysis.
- Error in sampling due to evaporative nature of HF, difficult to use pipettes

Determination of Fluoride

Some of the common methods used are

- Ion Selective electrode
- Spectrophotometry
- Ion Chromatography

Ion Chromatography

Ion Chromatography- inner view

Determination of Fluoride

Other methods used include

- Nuclear Magnetic Resonance Spectroscopy
- Raman Spectra

Each methods has its own advantages and disadvantages and require modification of procedures to meet the specific requirements.

Ion Chromatography provides a convenient and simple method for the determination of fluoride and sulphate together in a single analysis.

- Measures concentrations of ionic species by separating them based on their interaction with resin.
- Sample solutions pass through a pressurized chromatographic column where ions are adsorbed by the column constituents.
- Ion extraction liquid (eluent or Mobile phase) runs through the column to separate the adsorbed ions. The retention time of different species determines the ionic concentrations in the sample.
- During chromatographic separation, distribution equilibrium is formed between the mobile and stationary phases for each individual component.

$$D_A = [A]_s / [A]_M$$

Substances with large D will be retained more strongly than with smaller D and shown in the form of a chromatogram.

Detector signal (conductivity in this case) is recorded as a function of the elution volume of the mobile phase or time.

Instrument: Compact 861 Ion Chromatography System, Metrohm AG with Column Metrosep A Supp 5 – 250/4.0 Anion column

Column material: Poly vinyl alcohol with quarternery ammonium compounds, particle size 5 microns.

Mobile phase: sodium carbonate 3.32 mmol/litre and sodium hydrogen carbonate 1 mmol/litre.

Mixed standards were prepared using potassium sulfate and potassium fluoride.

Calibration of the instrument was carried out with known concentration of sulphate and fluoride.

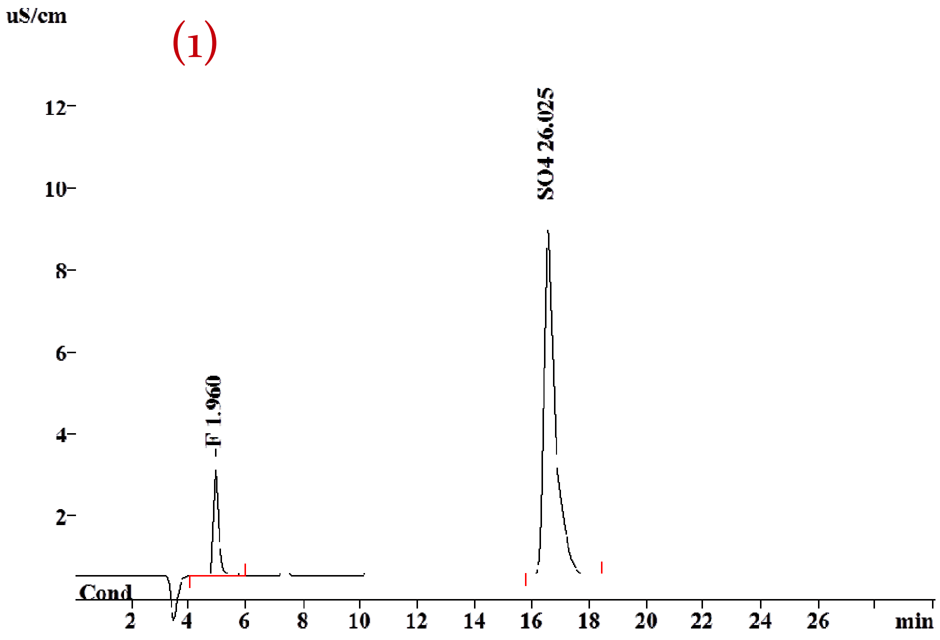
Sampling of EP solution by weight and diluting with water

(1) Calibration chromatogram for fluoride and sulphate

(2) Analysis of fluoride in HF

(3) Analysis of sulphate in H2SO4

(1)



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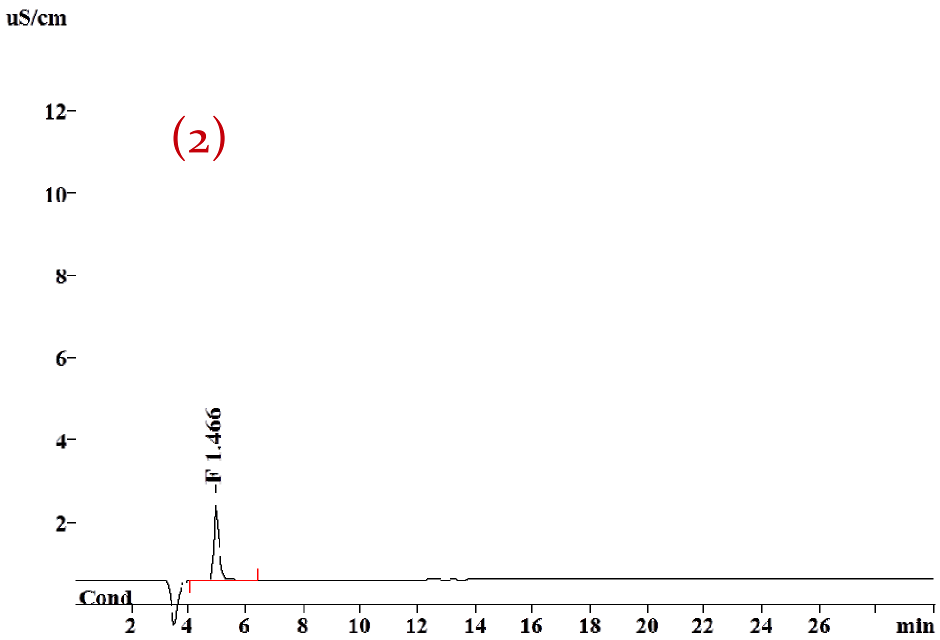

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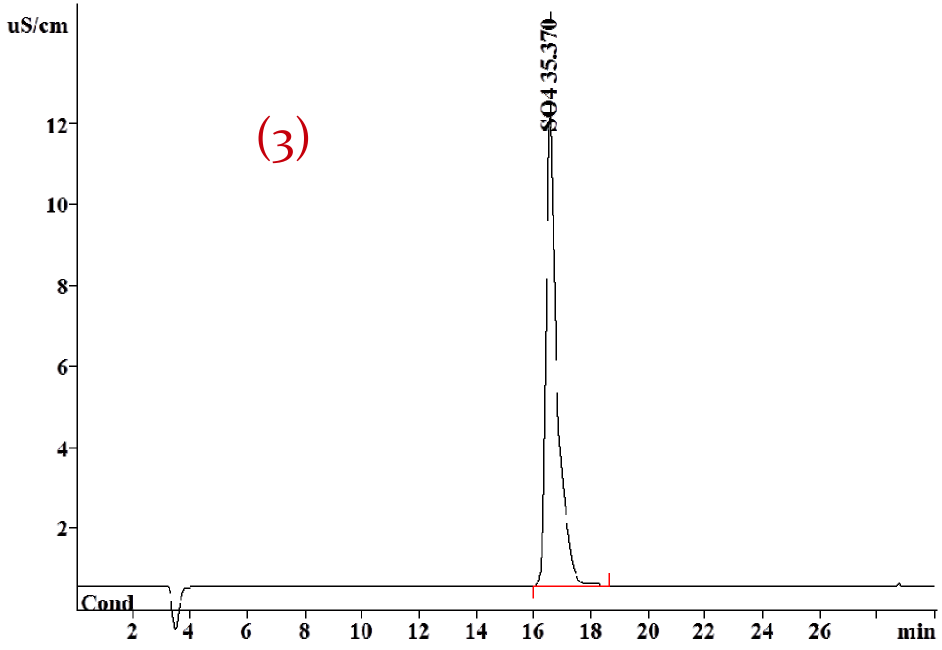
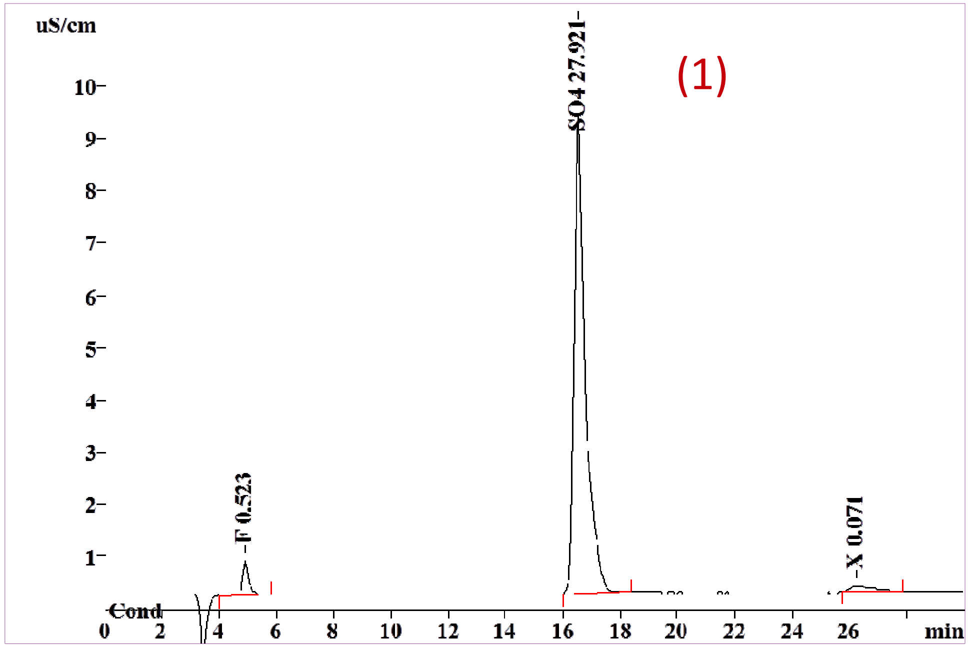
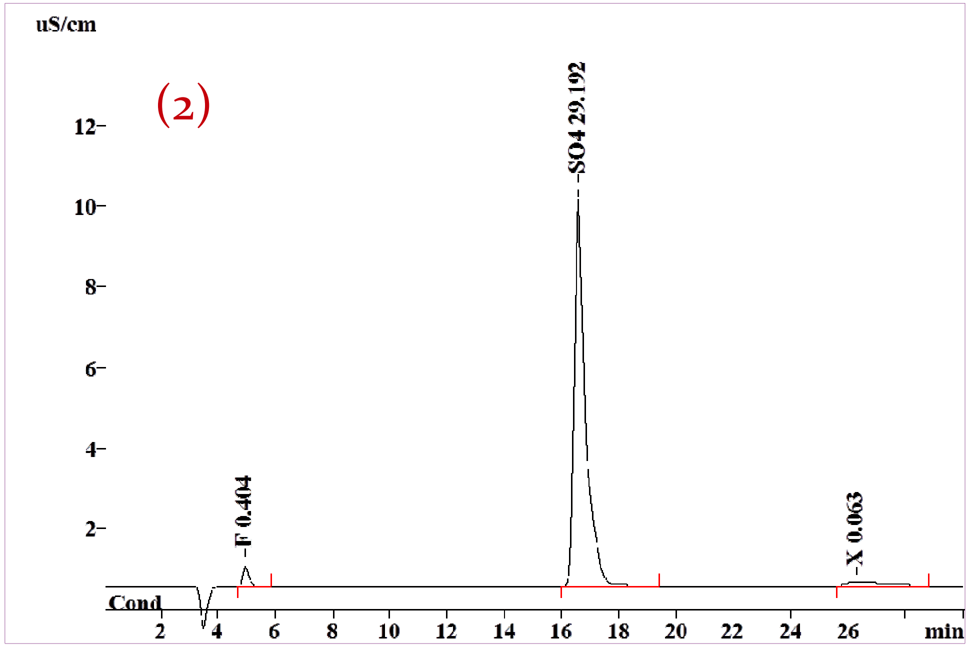


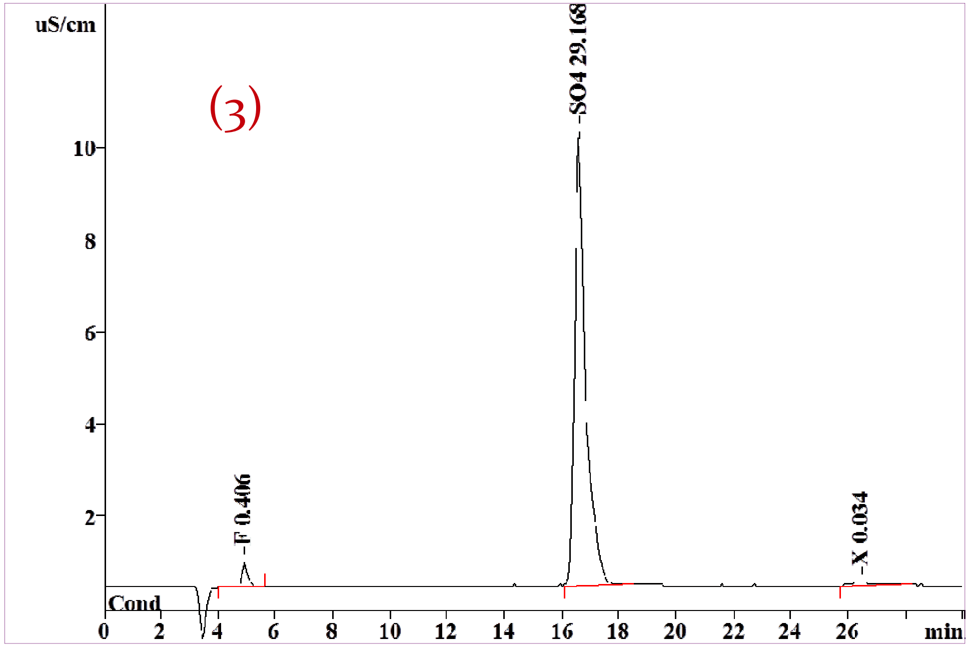
(1) Fresh EP solution

(2)After 15.3 hours EP

(3)After 36.3 hours EP







Well resolved and clear peaks for fluoride, sulphate and HSO_3F were obtained in mobile phase containing 3.2 mM sodium carbonate and 50 mM sulphuric acid.

Reduction in the concentration of fluoride and sulphate ions in fresh solution with respect to the expected values is due to the formation of fluorosulphonic acid.

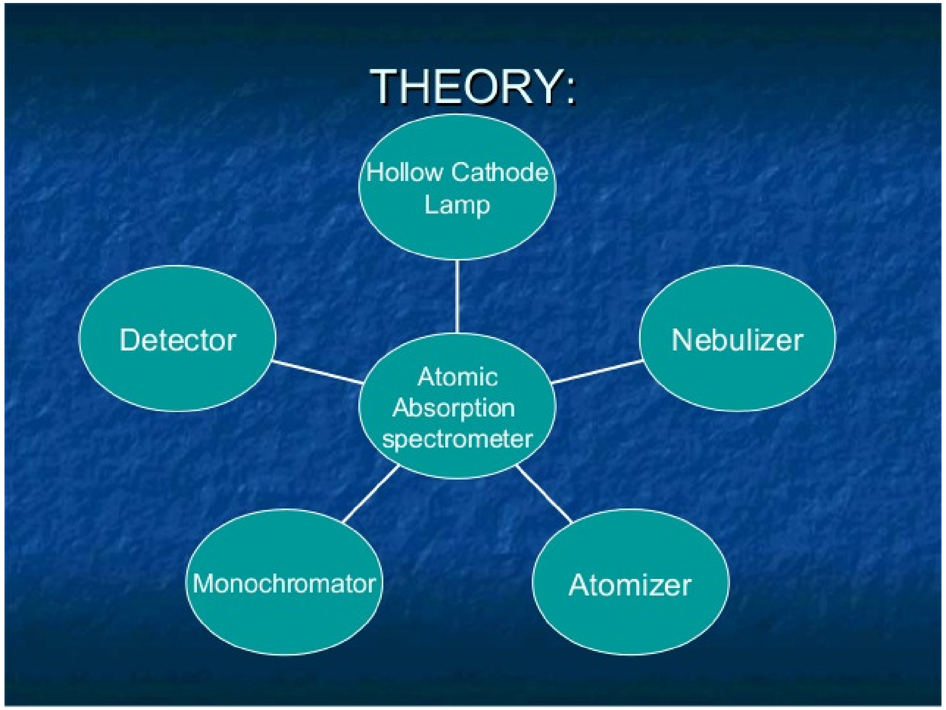
It is observed that the concentration of HSO_3F decreases with polishing time continuously whereas fluoride ion concentration decreased initially and thereafter remains constant.

Dissolved niobium utilizes available free F^- ions first, which is replenished in the solution by the dissociation of flurosulphonic acid.

On continuing further, the concentration of F^- ions remain unchanged while the HSO_3F concentration is reduced drastically.

Determination of Niobium

- Atomic Absorption Spectrophotometer (AAS)
- UV-Visible Spectrophotometry



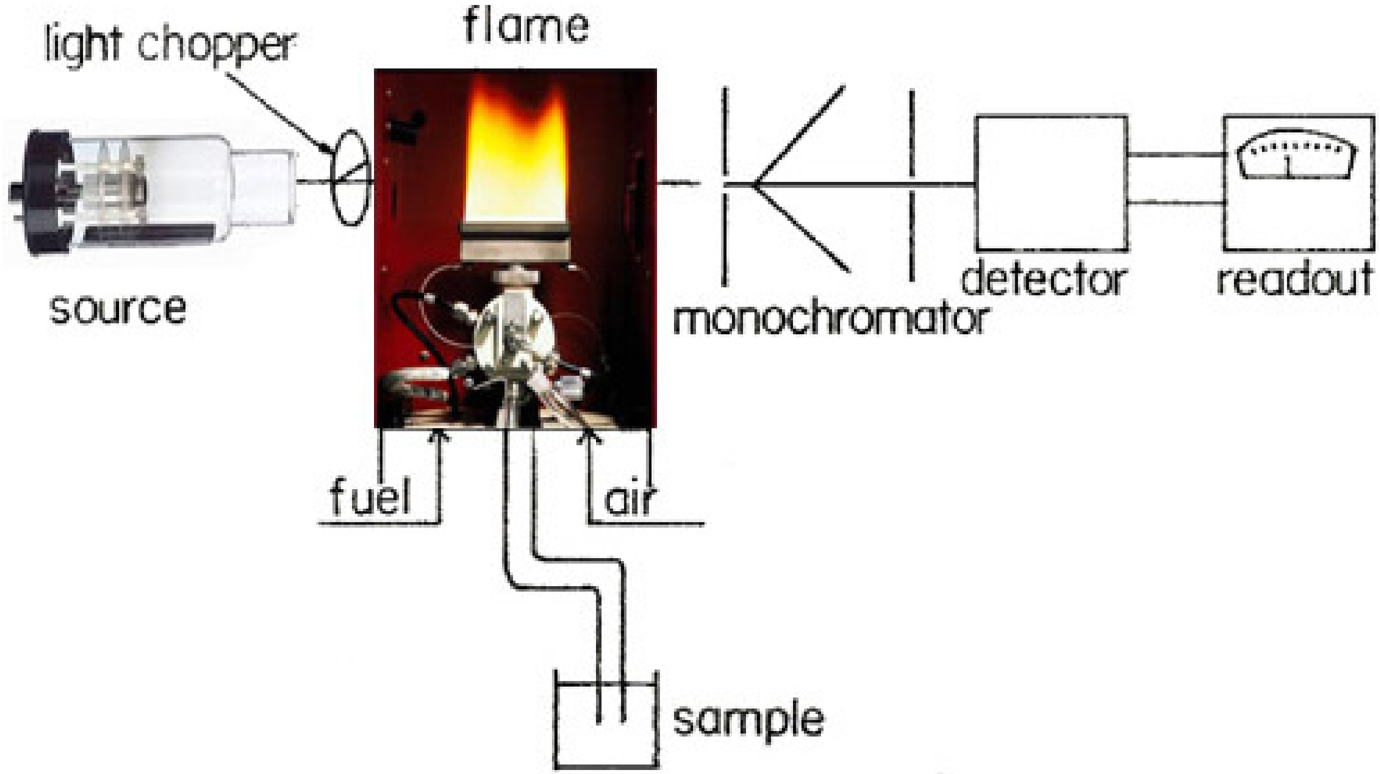
Atomic Absorption Spectrophotometer

AAS technique uses the principle that, free atoms generated in an atomizer can absorb radiation at a specific frequency.

AAS quantifies the absorption of ground state atoms in the gaseous state.

The atoms absorb ultraviolet or visible light and make transition to higher electronic levels. The analyte concentration is determined from the amount of absorption.

AAS requires an oxidant gas in addition to fuel gas. Air and nitrous oxide are used as oxidant gas in general.



Ref: Advanced strategies in food analysis, Atomic Spectrometry, Richard Koplik

The solution containing the element of interest is introduced into the flame along with the fuel and oxidant gas mixture in a pre-determined proportion.

NEBULIZER suck up liquid samples at controlled rate, create a fine aerosol spray for introduction into flame. Mix the aerosol and fuel and oxidant thoroughly for introduction into flame.

Two commonly used gas combinations:

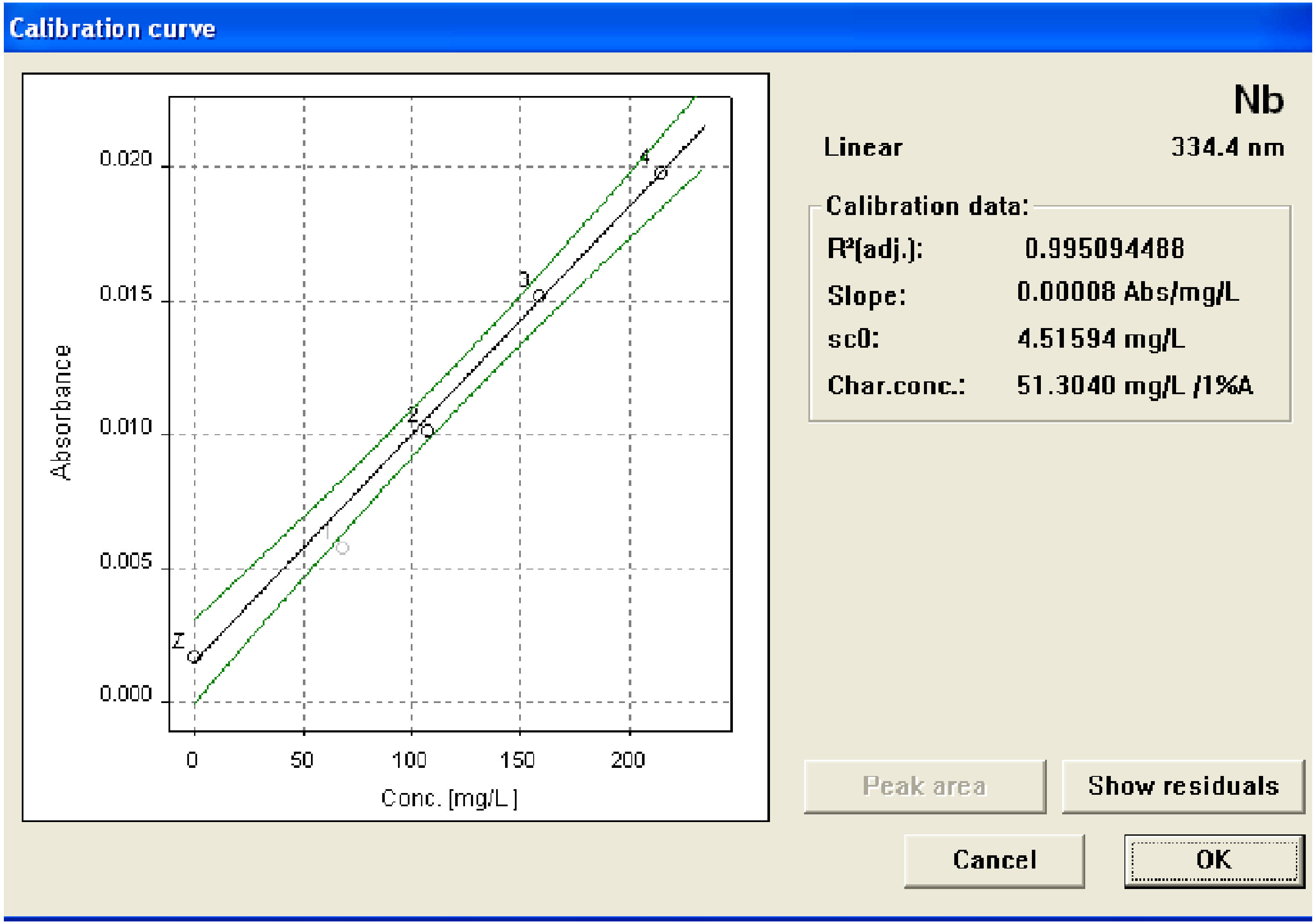
Air – acetylene (2150 – 2300ºC)
Nitrous Oxide – Acetylene (3000ºC)

The sample enters the flame as minute liquid droplets. Due to the high temperature of the flame the solvent evaporates first and solid salt or crystals remain. The solids melt instantaneously and molecular vapour is formed.

Thermal dissociation of bonds results in formation of ground state atoms of the element of interest .

It is these atoms that contribute to the absorption of the characteristic wavelength from the light source.

Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration.



Nb

Linear 334.4 nm

Calibration data:

R²(adj.): 0.995094488

Slope: 0.00008 Abs/mg/L

sc0: 4.51594 mg/L

Char.conc.: 51.3040 mg/L /1%A

Analytical features of AAS

- Sensitivity – sensitivity in Flame AAS is indirectly expressed as characteristic concentration (i.e. such concentration [μg/ml] of the element that gives the absorbance of 0.0044);
- Detection limits – in F AAS approx. 2 to 5 times lower than characteristic concentration.
- Working range – approx. 2 to 3 orders of magnitude (a narrower range in GF AAS).
- Repeatability – in F AAS under optimum conditions RSD 0.5-1.5 %; RSD in GF AAS ranges approx. from 1 to 5 %.
- Accuracy, trueness –accuracy can be affected by the sample matrix (e.g via analyte transport, formation of thermally stable compounds, non-atomic absorption).

Some problems (difficulties) of Flame AAS application

1. Partial ionization of some elements in the flame and non-uniform de-ionizing effect of the matrix

   Consequence: some loss of sensitivity, convex distortion of calibration curve, inaccurate results in the presence unknown amounts of other easily ionizable elements

   Solution: addition of a compound of an easily ionizable element (CsCl or KCl) in a large excess (CsCl 1-5 mg/ml)

2. Chemical interferences induced by the sample matrix resulting in the incomplete atomization of the analyte

   Consequence: e.g. negative bias of the results of Ca determination in phosphorus containing samples (all biological materials)

   Solution: addition of releasing agent ($LaCl_3$, La conc. up to 10 mg/ml) to the samples and standards (in air-C_2H_2 flame) or measurement in hot N_2O-C_2H_2 flame (addition de ionizing agent is needed).

Ultrapure Water Quality

- pH (pH meter, online/table top)
- Conductivity (Conductivity meter, online/table top)
- TOC (TOC analyzer online/table top)
- Hardness (Total, Mg) (titration)
- Iron (AAS, UV-Vis Spectrophotometer, ICP-OES, ICP-MS)
- Copper (AAS, UV-Vis Spectrophotometer, ICP-OES, ICP-MS)
- Nickel (AAS, UV-Vis Spectrophotometer, ICP-OES, ICP-MS)
- Silica (UV – VisibleSpectrophotometer)

All instruments cannot be used for trace level as such. However modification of sample preparation and standard additions can be employed for trace level analysis

Studies on treatment and disposal of used acids

Aim: To treat used electropolishing solution and its disposal.

- No recyclers are available for collecting the used acid .
- Response from external agencies to take up the design, installation and commissioning of the effluent treatment was not encouraging.

Probable Reasons:

- Small quantity of acid generated compared with the generation by industries.
- Literature for treatment of niobium electropolishing solution not readily available.
- Cost involved in setting up the ETP is less compared to preliminary studies that has to be carried out.
- Slim chances of getting the work order after doing the preliminary studies

Methodology:

1. Optimization of dilution factor

   (1) To avoid excessive heat during neutralization of strong acid and base.

   (2) To reduce the evaporation of hydrofluoric acid due to heat of neutralization

   (3) To bring the concentration of ions within the limits after treatment.

2. Removal of fluoride, sulphate and niobium by different methods based on its chemistry.

3. Establishment of analytical methods for monitoring the concentration of ions in treated and untreated effluent.

4. Separation of solid waste and its disposal

- Mixing of sulfuric acid and water to form a solution generally results in the evolution of heat.

- Enthalpy change per mole of any solute (in this case sulfuric acid) eventually becomes constant after certain dilution.

$$H_2SO_4(l) + Aq \dashrightarrow 2H^+(aq) + SO_4^{2-}(aq) \quad \Delta H = -96.2\ kJ/mol$$

- For 50 litre batch, volume of sulfuric acid is 45 litres (= 828 moles) and remaining HF. 50 litres will be diluted to 1000 litres with water.

- Dilution volume was kept to 1000 litres (dilution factor 25) to restrict the temperature change ($\Delta T = 25$ to $30\ ^\circ C$) .

- Three different treatment methods were adopted in the laboratory to identify its suitability for removing fluorides and sulphates.

- Only calcium hydroxide, calcium hydroxide + sodium hydroxide and sodium hydroxide + calcium oxide.

$$H_2SO_4 + Ca(OH)_2 \rightarrow 2\,H_2O + CaSO_4\ (ppt)$$

$$2\,HF + Ca(OH)_2 \rightarrow 2\,H_2O + CaF_2\ (ppt)$$

$$H_2SO_4 + 2\,NaOH \rightarrow 2\,H_2O + Na_2SO_4$$

- Sodium hydroxide was tested with the aim to reduce the hardness of water from excess calcium hydroxide used for raising the pH.

- Treatment with calcium hydroxide only was found more efficient in removing fluoride and sulphate compared to other two methods.

Effluent Treatment Plant for used EP Solution

CONCLUSIONS:

- Chemical, electrochemical processes and chemistry plays a crucial role in SRF cavity development.

- Niobium forms various compounds (simple and complex) with Nitric acid, Sulphuric acid, Phosphoric acid and hydro fluoric acid.

- Formation of complex compounds are beneficial in processing of cavities, whereas process control and treatment becomes difficult.

- Ion chromatography technique can be used for control of fluoride, sulphuric acid and fluro sulphonic acid in niobium electropolishing solution.

- More studies will be carried for accurate determination of niobium by AAS

- ETP facility for used Nb electropolishing solution based on laboratory studies has been installed and tested for its operation.

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