INTERNATIONAL MOTIVATION AND COOPERATION FOR RESEARCH IN THE ULTRA-HIGH PURIFICATION OF METALS

TAMÁS KÉKESI
Department of Non-Ferrous Extractive Metallurgy, University of Miskolc
3515 Miskolc-Egyetemváros, Hungary
fekkt@uni-miskolc.hu

[Received November 15, 2002]

Abstract: Due to the dramatic change in the properties as the last traces of impurities are removed, ultra-high purity metals can be considered to be new functional materials, which find dynamically growing applications in a number of specialized fields in modern technology, especially in electronics. Definition of purity levels requires sophisticated techniques. Direct analytical methods can hardly cover all the elements with high accuracy. Indirect methods – mainly by testing the residual resistivity at 4.2 K – are also demanding, but can offer a global index of purity if conditions of the material are standardized. Purification of metals by the conventional techniques may involve several steps of different treatment, often limited in efficiency. Separation of the impurities from the base metal dissolved in HCl solutions may be comprehensive and efficient by anion-exchange. Utilization of the significant differences in chloro-complex formation and ion-exchange sorption can result in the elimination of virtually all the significant impurities. Selectivity is achieved by the appropriate control of HCl concentrations and redox conditions during the ion-exchange procedure.

1. Introduction

The progress in modern technology has become a fundamental factor in determining the quality of life. The sustainable development of high technology fundamentally requires adequate materials. In this respect, various metals have been re-discovered and recognized as strategic materials of future technology provided they are purified to the required – often extremely high – levels. Although the major interest in ultra-high purity is generated by advanced technologies (e.g. electronics, high vacuum processes, cryogenics, etc.), extreme purification is also motivated by the theoretical and practical importance of determining the intrinsic physical properties of the pure material. True properties may be strongly distorted by seemingly negligible quantities of some impurities. One part of impurity in a million of the matrix metal can significantly influence physical properties [Kékesi and Isshiki, 2001]. The effect of a certain impurity can also strongly depend on the state of occurrence. Electric properties are influenced practically by impurities homogeneously dissolved in single-phase condition, while mechanical properties are strongly dependent on interstitially segregated impurities. Important properties of materials can be enhanced substantially by reducing the concentration of impurities to extremely low levels. It also implies that metals of ultra-high purity can be considered to be new functional materials.
The sensitivity of a property to the concentration and state of a chemical impurity or intrinsic structural defect depends on the nature of the property (electrical, optical and nuclear). Therefore, every field of application has its characteristic purity requirement. A substance is considered practically pure if its properties are determined by the atomic-crystalline structure and the intrinsic defects of the crystal lattice, while the relative effect of impurities is negligible [Kopeczky, 1986].

Although Hungary is not in the forefront of purity-related research, the availability of gallium in the Bayer liquor of alumina production has urged domestic research to develop extraction and purification technologies for this metal [Klug, 2002]. Ultra-high purity Ga serves as a fundamentally significant precursor for the GaAs semiconductor material, which has special properties, often placing it before silicon.

Combining long traditions with modern aspects in metal extraction and purification, the Department of Non-Ferrous Extractive Metallurgy at the University of Miskolc has offered a Hungarian contribution to the research of ultra-high purification of transition metals [Kékesi et al., 2002a]. This field had been exclusive to a few capable research centers in the USA, Japan or in France and Germany. Continued international cooperation, especially with the technically advanced Japanese partners at the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University is made possible by exploiting modern means of information exchange, state-sponsored mobility and appropriately tailored task-sharing.

2. Requirements and Determination of Metal Purity

Specialty-grade metals are primarily demanded in electronics, with copper having the most diverse applications in this field. The most common example is the material used for signal transmitting cables in electronics. Signal quality is recognizably better when the standard OFHC (Oxygen-Free High Conductivity Copper) material, containing 99.99% Cu is replaced with a specially refined stress free copper of approximately 6N (99.9999 per cent) purity [Miyake, 1992]. In a copper of this purity, the total amount of the impurities cannot exceed the total amount of 1 ppm (parts per million) by mass, approximately a hundred times less than in the case of the common OFHC grade. Other applications of ultra-high purity copper include the stabilizer cladding for low-temperature superconductors, high-vacuum gaskets and conductors for high-field magnets.

The plots in Fig. 1, constructed from a collection of published data [Kékesi, 1994], show the average changes of electrical resistivity as the concentration of a selected impurity is increased in solid solution in the copper matrix. The observed individual effects of the impurities are cumulative. Broken lines indicate the instability of the solid solution in the plotted range. The relatively small increase in resistivity caused by a second-phase impurity (0.004 ~ 0.01×10^-6 Ωcm per 100 ppm) is mainly attributed to the volumetric effect. Copper, however, exhibits a high capacity for holding a great number of elements in solid solution even at room temperature. Production of special grades implies the elimination of virtually all the impurities prior to casting the metal to formable shapes.
High purity metals are also required in practical use as constituent elements of compound semiconductors and as structural materials for ULSI (Ultra Large-Scale Integration) units. Besides gallium arsenide, the so-called II-VI compounds like zinc selenide or cadmium telluride have gained outstanding importance in modern electronics as established semiconductor materials. One of the current topics in the compound semiconductor field is focused on $\beta$-$\text{FeSi}_2$, a material for new opto-electronic devices in the infrared region. This, for example, directly represents a demand for semiconductor grade (high purity) iron. Commercial production of semiconductor grade silicon has long been practiced on a large scale. However, the lack of reliably efficient procedures for the ultra high purification of iron may impede the development of the new ecologically friendly semiconductor material. High purity cobalt is also promising as a basic component in gate electrode materials (cobalt silicide) in ULSI technology. Recent developments in magnetic recording technology have dramatically increased the demand for high purity iron, cobalt and chromium, which are the main ingredients in the active layers applied on magneto-optical mini-disks. Elimination of potentially radioactive impurities from the metals used for the preparation of integrated circuit elements is generally important in assuring reliability in computer technology.
Besides electrical resistivity, other physical properties may become important in special applications. Modern electronics industry is seeking materials to replace gold in IC (integrated circuit) bonding. Attention has recently been focused on special grades of copper. Points of particular importance in this application are: (a) shape, (b) softness and chemical inertness of the connecting ball. In all these respects, purity of the material plays a decisive role. From the point of view of mechanical properties, Figure 2 demonstrates that copper can replace gold in this application if sufficient softness is guaranteed by extensive purification. As in Fig. 2, the residual resistivity ratio (RRR) is often used as the measure of global purity. It expresses the ratio of the room temperature resistivity of a material to that at the temperature of liquid helium (4.2 K):

\[
\rho_B = \rho_T + \rho_D + \rho_i + \rho_s ,
\]

where \(\rho_T\) is the temperature dependent ideal resistivity component arising mainly from the thermal vibration of the lattice (phonon scattering), \(\rho_D\) expresses the effect of structural defects (vacancy, dislocation, grain boundary, etc.) disturbing the regularity of the lattice, and \(\rho_i\) is the contribution caused by the impurities in solid solution. Beyond the first three
principal terms, a further resistivity contribution may arise from the scattering of electrons by the surface of the metal, $\rho_S$, which has to be taken into consideration if the mean free path of the electrons, $\lambda$, becomes commensurate with the diameter, $d$, of the specimen [Thummes and Mende, 1974; Peterseim et al., 1979]:

$$\rho_S \approx \rho_{Bulk} C \frac{\lambda}{d},$$

(2)

where the parameter $C$ depends on the surface shape and only slightly on the $\lambda/d$ ratio and can usually be considered a constant.

The resistivity effect linked to the thermal vibration of the lattice is primarily important at higher temperatures but it vanishes below 10 K and the dependence of resistivity on temperature becomes negligible for pure materials at temperatures lower than 4 ~ 5 K [Isshiki and Igaki, 1978]. In the case of magnetic metals, a magneto-resistivity term has to be allowed for, due to the spontaneous magnetic field in the material. During material testing, however, this effect is usually avoided by superimposing an external (longitudinal) magnetic field.

Due to the additivity of the contributions, expressed in eq. (1), resistivity of the metal sample can be reduced to that caused by the impurities $\rho_i$:

$\rho_T$ vanishes at temperatures close to 0 K,

$\rho_D$ can be diminished by preliminary annealing,

$\rho_S$ can be determined by varying the diameters of the samples, although for comparative assessment this factor can be eliminated by keeping the dimensions constant and generally as large as technically possible.

The temperature provided by liquid helium (4.2K) has become generally accepted as the low temperature point to express the residual resistivity ratio:

$$RRR = \frac{\rho_{298}}{\rho_{12}} = \frac{R_{298}}{R_{4.2}}.$$  

(3)

With good approximation, this ratio can also be expressed with the directly measurable resistance of the sample at the two set temperatures. Levels of purity may be indicated by the changes in the residual resistivity only if all the impurity content is homogeneously dissolved in the base metal matrix. The effects of segregation or precipitation may lead to a false assessment of chemical purity. The use of residual electric resistivity for such purposes requires appropriate preparation and measuring techniques, assuring the proper state of the impurities and excluding any further reactions, especially internal oxidation.

Purity levels achieved in different laboratories and of different metals are compared practically by RRR results. Reported values, and corresponding processes are listed in Table 1. Purity evaluation by the RRR results is, however, uncertain in some cases, due to
the unspecified or improper sample preparation. Purity is correctly indicated in those cases when the purified and formed material has been subjected to hydrogen annealing for sufficient time before RRR testing, and the size effect has been corrected for. Due to the large differences in the chemical properties of the base metals, the tabulated RRR values show great differences.

<table>
<thead>
<tr>
<th>Group</th>
<th>Me</th>
<th>RRR_{1.2K}</th>
<th>Purification method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ib</td>
<td>Cu</td>
<td>36,000 (bulk)</td>
<td>6N-&gt; FZM, under reduced H₂ atmosphere</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>40,000 (single cr.)</td>
<td>6N-&gt;FZM in He + internal oxidation</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>&gt; 10000</td>
<td>Vacuum annealing</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7,000</td>
<td>RRR 140 -&gt; Annealing under reduced O₂ atmosph.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10,000 (single cr.)</td>
<td>Internal oxidation</td>
</tr>
<tr>
<td>IIA</td>
<td>Mg</td>
<td>3,200</td>
<td>Sublimation + zone melting</td>
</tr>
<tr>
<td></td>
<td>Ca</td>
<td>148</td>
<td>HP oxide -&gt; Al-reduction in vac. + vac. distillation</td>
</tr>
<tr>
<td></td>
<td>Sr</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ba</td>
<td>1,100</td>
<td></td>
</tr>
<tr>
<td>IIB</td>
<td>Zn</td>
<td>50,000 (single cr.)</td>
<td>FZM in H₂ atm. (Bridgeman method)</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>25,600</td>
<td>Vacuum distillation + zone melting</td>
</tr>
<tr>
<td></td>
<td></td>
<td>41,600 (single cr.)</td>
<td></td>
</tr>
<tr>
<td>IIIA</td>
<td>Y</td>
<td>1,200</td>
<td>Electrotransport</td>
</tr>
<tr>
<td></td>
<td>Nd</td>
<td>120 (RRR_{1.2K})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>La</td>
<td>260</td>
<td></td>
</tr>
<tr>
<td>IIB</td>
<td>Al</td>
<td>90,000 (bulk)</td>
<td>Electrolysis + fract. crystallization + zone melting</td>
</tr>
<tr>
<td></td>
<td>Ga</td>
<td>128,000 (bulk)</td>
<td></td>
</tr>
<tr>
<td>IVa</td>
<td>Ti</td>
<td>155</td>
<td>Deoxidation by Ca Hydroflux method</td>
</tr>
<tr>
<td></td>
<td>Zr</td>
<td>600</td>
<td>EBFZM + electrotransport</td>
</tr>
<tr>
<td></td>
<td>Hf</td>
<td>15</td>
<td>Decomp. of iodide + arc melting + electrotransport</td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>15,900 (bulk)</td>
<td>Zone melting</td>
</tr>
<tr>
<td>IVb</td>
<td>V</td>
<td>1,880</td>
<td>Electrorefining + arc melting + electrotransport</td>
</tr>
<tr>
<td></td>
<td>Nb</td>
<td>24,500</td>
<td>Electrorefining + EBFZM + UHV annealing</td>
</tr>
<tr>
<td></td>
<td>Ta</td>
<td>8,000 (single cr.)</td>
<td>EBFZM + UHV annealing</td>
</tr>
<tr>
<td>Vla</td>
<td>Cr</td>
<td>667</td>
<td>FZM + H₂ annealing</td>
</tr>
<tr>
<td></td>
<td>Mo</td>
<td>&gt; 700</td>
<td>Electrotransport (in Zr foil)</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>9,000 (single cr.)</td>
<td>EBFZM + red. pres. O₂ annealing + UHV annealing</td>
</tr>
<tr>
<td></td>
<td></td>
<td>86,000</td>
<td>EBFZM</td>
</tr>
<tr>
<td>VIII</td>
<td>Fe</td>
<td>20,210 (RRR₀K)</td>
<td>AIEEX + FZM + H₂ annealing</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>334</td>
<td>AIEEX + electrolysis + FZM + H₂ annealing</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>7,000</td>
<td>AIEEX + electrolysis + H₂ annealing + EBFZM</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>5,000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>&gt; 25,000 (bulk)</td>
<td>FZM in air (internal oxidation)</td>
</tr>
</tbody>
</table>

Table 1. Reported RRR values of high-purity metals [T. Kékesi and M. Isshiki, 2001].
(FZM - Floating Zone Melting, HP - High Purity, UHV - Ultra High Vacuum, red. - reduced, cr. - crystal)

The purity of a metal may be evaluated conventionally by direct chemical analysis. Probably the most advantageous direct and universal method of providing a virtually complete analysis of high purity metals is Glow Discharge Mass Spectrometry (GDMS).
Sensitivity is very high, and contamination is excluded by generating the ions directly on
the appropriately prepared solid metal samples. Another efficient method is activation
followed by gamma-ray spectrometry. Activation analysis, based on irradiation by γ-ray,
neutrons or charged particles, is the sensitive analytical method to be applied to the non-
metallic elements [Isshiki et al., 1984]. Direct analytical results are most often incomplete
since not all impurities can be analyzed. For commercial purposes, therefore, the term
nominal purity is frequently used, meaning that some selected impurities are analyzed, but
others are not accounted for. This shortcoming is aggravated usually by the precision and
detection limit factors, strongly depending on the method and the operator.

As suggested by Fig. 1, impurities may have very different coefficients of influence on
electrical resistivity. Therefore, exact impurity assessment is possible in the case of samples
obtained by the same purification procedure, exhibiting the same - or similar - relative
impurity concentrations. In other cases, the use of low temperature resistivities requires the
analytical data of the major components as well.

3. Potential Methods of Ultra-High Purification

Purification techniques in general utilize the differences in physicochemical properties of
the base metal and the impurities, in removing the latter to a second phase adjacent but
immiscible with the one containing the base metal. The commonly applied methods are
indicated in the compilation of Table 1. The procedures of different nature can be classified
according to the main property chosen to be utilized in separation. The most common
examples are selective reaction of the impurities forming a compound, which is not
dissolved in the base metal. The differences in electrode potentials are utilized for further
purification by electrolysis. The chemical techniques can be complemented with physical
procedures aiming at the segregation of impurities during fractional crystallization or
achieving separation by selective evaporation. Conventional purification of metals to the
part per million levels cannot be carried out by a single method. As outlined in Figure 3, the
desired level of purity can be assured by a sequence of complementary refining steps.
Aqueous precipitation techniques are suitable for removing large quantities of different impurities, as applied in commercial hydrometallurgical operations, but under appropriate conditions they can also be applied to fine purification. In order to achieve ultra high purity, however, further ion selective methods have to be applied in the solution phase. The metal is usually extracted from the purified solution by electrolysis or hydrogen reduction of the crystallized and dehydrated salt. Remaining traces of impurities can be eliminated by controlled potential electrolysis or by different physical methods. The purified metal is annealed in ultra high vacuum followed by several steps of mechanical shaping and annealing. Concomitant superficial contamination is removed by repeated chemical or electrochemical polishing.

Solution pre-treatment, based on a combination of different precipitation techniques, may eliminate significant amounts of impurities from solutions. Conventional aqueous purification processes of solutions containing a number of impurity elements may become rather complicated, involving cumbersome consecutive steps of precipitation and filtration.

On the other hand, the base metal and the impurities can be separated efficiently in the solution as dissolved ions. This approach is made possible by the availability of organic materials of ion-exchanging properties. These special organic materials, constituting the cation or anion exchange resins and liquid extractants, always contain mobile counter-ions (\(C^+\) cations or \(A^-\) anions), which may be exchanged for the corresponding aquated or complexed ions of the metal (\(Me^{n+}\) or \(\left[MeX\right]^{n-}\)) in solution. The generalized reversible reactions for the cation and anion exchanges, respectively, are expressed:

\[
\left[MeX_{\alpha}\right]^{(n-\alpha)+} + (n-\alpha)(R \cdot C) \Leftrightarrow (n-\alpha)R \cdot MeX_{\alpha} + (n-\alpha)C^+,
\]

or

\[
\left[MeX_{\beta}\right]^{(n-\beta)-} + (n-\beta)(R \cdot A) \Leftrightarrow (n-\beta)R \cdot MeX_{\beta} + (n-\beta)A^-,
\]

Separation of metal ions in solution can be effected by applying selective sorption and/or elution. This is carried out by adjusting the chemistry of the aqueous solution in a way that favours selective uptake or release of one metal by the organic phase. The degree of separation in a single batch operation is limited by the equilibrium distribution coefficients. Conditions of perfectly selective sorption and elution are impossible. Nevertheless, efficient purification is attainable by chromatographic elution, which is physically possible when ion-exchange columns are used. Column operations can be regarded as a large number of repeated batch equilibration steps. The eluent solution, used to rinse the ion-exchange column, may desorb metals at different rates, forming elution fronts, which are moving at different rates. The selected metal is obtained in a certain volume fraction of the effluent, highly purified from the rest of the metals. Therefore, overall purification of solutions, elimination of the largest possible number of impurities, requires passing the solution through an ion-exchange resin bed contained in a vertical column, followed by feeding the appropriate eluent solution at an adequate rate.
The separating effect of ion-exchange can be enhanced greatly by applying aqueous media
where the metal ions may be complexed, some of them forming anionic species. The
negatively charged complexes are subject to sorption of different strengths on anion
exchange resins. The stability of metal-complex species may show great differences [Sillen
and Martell, 1964] and depend on the concentration of the complexing anions in the
solution, according to the following equilibrium:

\[
[Me(H_2O)_y]^{n+y-} + xCl^- \rightarrow [Me(H_2O)_{y-x}Cl_x]^{n-x}
\]  

Application of a strongly basic anion exchange resin (usually of the quaternary amine type
functional groups on a polystyrene-divinilbenzene matrix) and a complexing aqueous
medium can offer generally the highest efficiencies of purification. Those metals not
forming anionic complex species can be directly separated if the selected metal is strongly
complexed and sorbed under the applied conditions.

The most effective and common complexing agent in aqueous solutions is chloride ion.
Chloro-complexes of a large number of metals can be formed at appropriate concentrations
of HCl in the solution. For the purpose of ultra high purity, it is best to avoid the
introduction of foreign metals; therefore, the complexing chloride ions are supplied in the
form of pure hydrochloric acid. Hydrochloric acid is an ideal medium also from the point
of any residual contamination, because its components are readily removed during the final
melting of the purified metal. The tendency of an element to form chloro-complex species
also depends on the oxidation state \((n^{+})\) of the ions. Therefore, application of properly
controlled oxidation states is an important tool for enhancing anion-exchange separation of
metals in HCl solutions.

4. Designing and Testing of Anion-Exchange Separations

To assist in designing the anion-exchange separations, a computer simulation program has
been constructed which can assess redox and chloro-complex formation equilibria in HCl
solutions. The algorithm expresses the activities of the species with the activity of the aqua
species in the lowest oxidation state \((a_{Me^{n+}})\):

\[
a_{MeCl^{n+}} = f(a_{Me^{n+}}) = \beta_{n-x} \cdot \left(\frac{c_{Cl^-} \cdot E_{n-x/n}^{+}}{a_{Me^{n+}} \cdot 10^{-\gamma_a}}\right)
\]  

where \(c_{Cl^-}\) is the chloride ion concentration, \(\gamma_a\) is the mean activity coefficient of the HCl
solution, determined by the overwhelming excess of hydrochloric acid [Zemaitis et al.,
1983]. The cumulative stability constant [Sillen and Martell, 1964] referring to the
\([MeCl_x]^{n-x}\) chloro-complex species is denoted by \(\beta_{n-x}\). The standard redox potential
belonging to the aqua species of adjacent oxidation states \((n, n+1)\) in a series is denoted by
\(E_{n+1/n}^{+}\), and the redox potential enforced on the system by the added agent is \(E\) [Sillen and
Results of simulation are demonstrated by the examples of Fig. 4, showing the estimated concentrations of the copper species in equilibrium with metallic iron, added to the HCl solution as a reducing agents in the particulate form. The computed results can predict possible precipitation reactions.

![Graph showing copper species dissolved in HCl, in equilibrium with solid Fe](image)

Figure 4. Copper species dissolved in HCl, in equilibrium with solid Fe

Anion-exchange equilibria were tested experimentally by the method of batch equilibration. Distribution of a large number of metals was investigated at varied HCl concentrations, under controlled redox conditions (Fig. 5).

![Diagram showing experimental procedure](image)

Figure 5. The experimental procedure used for the determination of the ion-exchange distribution coefficients
Reduction was carried out - if needed - by stirring the solution with the fine powder of a suitable metallic element (Zn, Co, Fe or Cu) as reducing agent, in a reactor purged with nitrogen gas. Alternately, the highest practical oxidation states were stabilized by adding hydrogen peroxide. Solution samples of various HCl concentrations were prepared by mixing equal volumes of the stock solution with varied volumes of concentrated HCl and de-ionized water.

Strength of sorption is practically characterized by the equilibrium distribution coefficient, expressing the ratio of the equilibrated metal ion concentration in the organic (resin or liquid) phase ($c_{\text{e,res}}$) to the corresponding concentration in the aqueous solution ($c_{\text{e, sol}}$). The anion-exchange distribution coefficients were determined from the analytical results of the examined metal in the initial ($c_{\text{e,sol}}$) and in the equilibrated solutions:

\[
D = \frac{c_{\text{e,res}}}{c_{\text{e,sol}}} = \frac{V_{\text{sol}}(c_{\text{e,sol}} - c_{\text{e,sol}})}{V_{\text{res}} c_{\text{e,sol}}} \quad (8)
\]

The results of the equilibrium experiments are summarized in Figure 6 for the most important cases. Distribution coefficients of Mn(II), Cr(III), V(IV) and V(V) did not exceed unity significantly in the examined 0 - 10 M HCl range, therefore they have not been plotted in Fig. 6. Similarly, the alkali and alkaline earth metals and the elements in the first two rows of the p-block in the Periodic Table have no distribution functions, because they are unable to form sorbable anionic chloro-complex species [Kraus and Nelson, 1956].

The great differences in sorption characteristics of the elements in hydrochloric media suggest that an optimum elution process, applying different concentrations of HCl for rinsing, may be compiled for the overall purification of the majority of base metals [Kékesi et al., 2000b]. Proper adjustment of the HCl concentration in the eluent fractions requires elution experiments with bench scale columns.

The formation of the chloro-complex anions was confirmed also by examining the visible light absorption spectra. As it is demonstrated with the example of iron(III) in Fig. 7, spectral changes caused by the increase in the HCl concentration can be interpreted by the relevant changes in the observed anion-exchange distribution coefficients. The appearance of the double peak at the ~315/~375 nm wavelengths as the HCl concentration is increased reflects the gradual stabilization of the anionic chloro-complex species, causing a concurrent rise in the anion-exchange distribution function (Fig. 6). Spectrophotometry was used also for detecting the changes in the oxidation states of an examined element dissolved in HCl solutions [Kékesi et al., 2000b]. The reduction or oxidation of the metal ion in the complexes transforms the light absorption spectrum.

Separations were devised according to the established anion-exchange distribution functions of Fig. 6, complemented by earlier data [Kraus, 1956] and the results of thermodynamic simulation. The general procedure is shown in Figure 8. If reduced conditions are mandatory for the elimination of an impurity element, the powder of the
main element, as a reducing agent, is stirred in the starting solution, while the reactor is flushed with nitrogen gas. In practice, the first effluent should be loaded to a second ion exchange column for a subsequent separation step as after oxidation. Separations under oxidized (or air-stable) conditions, however, were tested independently. When the main metal is strongly fixed in the resin bed under reduced conditions, the elution may be enhanced and separation sharpened by converting it to a higher oxidation state [Kékesi, 1997a]. In situ oxidation of the sorbed species in the resin phase can be affected by applying calculated amounts of hydrogen peroxide.

Figure 6. Anion-exchange distribution functions determined by batch equilibration
Figure 7. The effect of HCl concentration on the Fe(III) absorption spectrum

Figure 8. The general flow-sheet of an anion-exchange separation procedure
The procedures of separation are demonstrated through the example of iron purification. According to Fig. 6, confirming earlier findings [Isshiki and Igaki, 1978], separation of divalent copper from trivalent iron in chloride media poses great difficulties. However, monovalent copper is firmly fixed in the resin and iron is directly eluted in the Fe(II) form at 1.5~2 mol dm$^{-3}$ HCl concentration, as demonstrated by the elution curves in Fig. 9.

In agreement with the simulated results shown in Fig. 4, the reducing pre-treatment of the starting solution has an additional purifying effect, as the original impurity copper content can be significantly reduced by precipitation on the added iron powder. Although the main purpose of the first anion-exchange step is to eliminate the residual copper from the treated starting solution, a number of other impurities are also removed by sorption.

On the other hand, many other important impurities (not forming anionic chloro-complexes) can only be eliminated if iron is fixed in the Fe(III)-chloro complex form, which can be safely achieved at > 5 mol dm$^{-3}$ HCl concentration. Therefore, the combination of two separation steps in the Fe(II) and Fe(III) oxidation states is indispensable. Figure 10 shows the characteristic elution functions of the second step of the combined anion-exchange procedure.

![Figure 9](image-url)  
Figure 9. The first step in the anion exchange separation procedure for iron purification (Loading and elution under reduced conditions: monovalent copper and divalent iron)

In the course of optimizing a separation procedure, the elution curves obtained can be numerically integrated to express the purification ratio ($PR$):
of an impurity and the yield of the main element:

\[ Y = \frac{100\% \cdot \int_{V_s}^{V_e} c_m dV}{\int_{V_s}^{V_e} c_m dV} \times V \]

where \( V_s \) and \( V_e \) are the effluent volumes at the starting and ending points of the purified solution collection, respectively. The loaded amount of the impurity is \( \Sigma m_i \) and that of the main element is \( \Sigma m_m \). The amounts collected in the purified solution are \( m_i \) and \( m_m \), as determined from the corresponding concentrations \((c_i \text{ and } c_m)\). Computed ratios of purification may refer to different intervals of effluent collection, i.e., different widths \((V_e - V_s)\) of the principal elution peak:

\[ c_m \geq c_{m,\text{max}} / k \]

Standard purification ratios \((PR_{i,\text{std}})\) referring to the volume range defined by the half-height concentrations of the main element (where \( k = 2 \) for both the initial and the final concentration values of the collected portion) are higher than 1000 for most of the characteristic impurity elements, in the combined iron purification process. The first anion-exchange step enhanced the removal of copper after the major part of the copper concentration had been precipitated by the preliminary reducing treatment. In the second anion-exchange step, the standard purification ratio of silicon was higher than 100, however, that of cobalt was less than 100. It can be improved by a third step of anion-exchange separation optimized specifically for the elimination of cobalt. Elimination of molybdenum during the second step required the application of hydrogen peroxide in the influent solutions, which prevented the reduction of Mo(VI) to Mo(V). In accordance with the functions in Fig. 6, the latter form could not be retained in the resin while Fe(III) was eluted with ~ 1M HCl.

The standard value of yield is ~ 90 % in the first step and ~ 55 % in the second. The yield can be increased by collecting a larger portion of the purified effluent, but in this case some impurities (Co, Si, Ti) may be less perfectly removed. The characteristic indexes of purification, referring to different widths of effluent collection, are given in Table 2 and Table 3. The tabulated figures were determined with a computer program (ANEL) specifically developed for the analysis of elution test results. This program is capable of selecting the best wavelength used in the ICP (Inductively Coupled Plasma Atomic Emission Spectrometry) analysis of an element, and it carries out multiple corrections (interference, machine stability, HCl concentration difference) on the raw analytical data.
Figure 10. Characteristic elution curves of the second step in the anion-exchange separation procedure for iron purification (Loading, acid rinsing and elution under oxidised conditions applying 0.3 – 0.5% H₂O₂)

Table 2. Efficiency characteristics of the first step in the anion-exchange separation procedure for iron purification

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Fe</th>
<th>Cu_AIEX</th>
<th>Cu_Total</th>
<th>Sn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average load, mg</td>
<td>1985</td>
<td>0.150</td>
<td>22.60</td>
<td>18.55</td>
<td>18.48</td>
</tr>
<tr>
<td>1/10c₉Fe,max-1/10c₁₀Fe,max (VE = 69.4%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yield (Y), %</td>
<td>87.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purification ratio (PR)</td>
<td>-</td>
<td>19.68</td>
<td>&gt;1000</td>
<td>&gt;1000</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>1/10c₉Fe,max-1/10c₁₀Fe,max (VE = 80.7%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yield (Y), %</td>
<td>96.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purification ratio (PR)</td>
<td>-</td>
<td>19.21</td>
<td>&gt;1000</td>
<td>&gt;1000</td>
<td>&gt;1000</td>
</tr>
</tbody>
</table>

Cu_AIEX - copper eliminated by anion exchange,
Cu_Total - total amount of copper eliminated (by precipitation and anion exchange),
VE - volume efficiency (relative volume of the solution collected during separation)
Equilibrium distribution experiments have resulted in new or corrected anion-exchange sorption functions for a number of elements in various oxidation states. This fundamental information was used for the development of several anion-exchange separation procedures. The large-scale diversity in the formation and sorption characteristics of chloro-complex species has enabled the elimination of virtually all the significant impurities from several transition metals, demanded in ultra-high purity by practical applications. Reduction of the starting solutions with the pure powder of the metal to be purified proved to be an indispensable technique to separate certain impurities. A subsequent anion exchange step under oxidized conditions may result in the separation of the rest of the elements. Elution of elements strongly sorbed under reducing conditions could be enhanced by *in situ* oxidation. The aimed separations could be effected by the variation of the HCl concentration in the influent. The numerical analysis of the experimental elution curves could provide indexes to characterize the separations and for the optimization of the separation procedures. The results have demonstrated the feasibility of anion-exchange separation to be used for the preparation of ultra-high purity Fe, Co, Cu and Zn. The method can be expanded to the purification of further elements, as continued
investigations provide further results. Extraction of the metal from the purified solution is possible by tested alternative methods.

Acknowledgment: This research has been jointly supported by the Japan Society for the Promotion of Science and the Hungarian Scientific Research Fund (OTKA) under the project No. T037550. Further support has been received from the Normative Research Fund of the Department of Nonferrous Metallurgy, University of Miskolc.

List of references