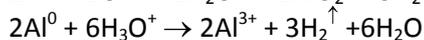
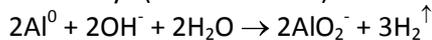


Classical qualitative analysis. 4. Alloys analysis

Alloys are mixtures or metallic solid solutions composed of two or more elements. In alloys one can distinguish the matrix (base metal) - metal, which content is the largest, as well as enriching admixtures. Depending on the nature of the matrix it can be distinguished:

1. light alloys:

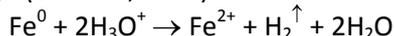
a) aluminium alloys (duraluminium) – the matrix can be dissolved in bases and acids (amphoteric)



b) magnesium alloys (magnalium) – the matrix can be dissolved in non-oxidizing acid



2. iron alloys (cast-iron, steel)

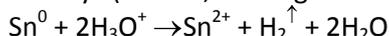


3. non-ferrous alloys

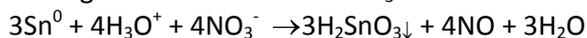
a) copper-base alloys (brass, bronze) – can be dissolved in dilute HNO_3



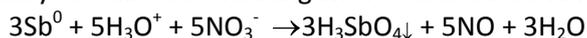
b) tin-base alloys (bronze, bearing metals) – can be dissolved in HCl (very slowly)



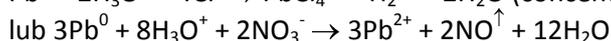
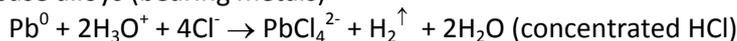
or heating with concentrated HNO_3



if alloy contains Sb – heating with concentrated HNO_3



c) lead-base alloys (bearing metals)



In order to determine the group to which a given alloy belongs, it should be checked alloy behavior in different solvents. On the surface of alloy one should put a drop of ~~solution~~ of given solvent (e.g. NaOH) and observe if dissolution reaction occurs. It can be also performed on the surface of the alloy, previously known identification reactions (introducing drops of appropriate reagents) (exercise 2). To quantitate the presence of metal dopants in alloys, instrumental methods (e.g. ICP) may be used.

Inductively coupled plasma-Atomic Emission Spectroscopy (ICP-AES)

ICP- AES is an emission spectrophotometric technique, exploiting the fact that excited atoms emit energy at a given wavelength as they return to ground state after excitation by high temperature argon plasma. The fundamental characteristic of this process is that each element emits energy at specific wavelengths peculiar to its atomic character (characteristic line spectra). An atom is a system which may absorb energy, but only in predetermined amounts (quantum of energy), what is precisely defined by energy level diagram. After energy absorption the outer-shell electron (or more electrons) are moved from lower to higher energy level. An excited atom, after very short time (of the order of nanoseconds or less) spontaneously returns to its ground state (in one step or in several intermediate steps) emitting radiation which is unique to each element. The intensity of radiation emitted at specific wavelength, is also characteristic for particular atom and depends on the concentration.

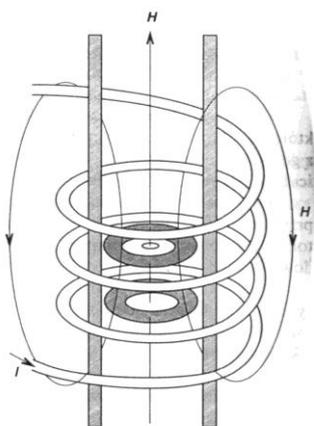
In ICP-AES method, the inductively coupled argon plasma is used as the excitation source. Plasma - hot system ($T > 1000 \text{ K}$) in the gaseous state, including the atoms and ions in the various excited states, free electrons, and the molecules, radicals, molecular ions, solid or liquid particles.

Plasma is generated by high-frequency magnetic field induced by copper coil and the flowing argon gas (argon-chemically inert gas, having a high first ionization energy of 1521 kJ/mol – effectively ionizes almost all elements, it is optically transparent). The argon gas is ionized in the intense electromagnetic field and created seed electrons and ions flow in ununular path. The electrons accelerate and encounter resistance through collision with argon atoms. This process occurs almost instantaneously leading to the generation of high temperature plasma ($6000\text{-}10000 \text{ K}$).

The sample solution is carried into the argon plasma in the form of aerosol obtained in nebulization process (using nebulizers). In hot plasma the following cycle takes place: vaporization of the solvent, dissociation of

molecules (atomization), excitation of the free atoms. The relaxation of the excited electrons as they return to the ground state is accompanied by the emission of photons of light with an energy characteristic of the element.

Inductively coupled „plasma torch”

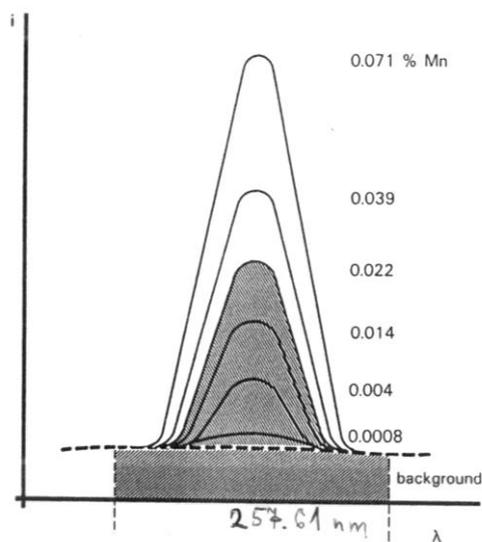


The emitted radiation is sent into a spectrometer, where it is split into individual lines by grating. Finally the emission is detected with photomultiplier detectors, which are coupled with computer.

ICP-AES is very useful analytical technique used for the detection of elements in a variety of natural samples in the solution form. The detection limit is good and for most elements is in the range of 0,1 - 10 ppb.

For semi-quantitative determination of metal dopants in the alloy by ICP method the measurement should be

performed at specific wavelength, characteristic for a given atom (or molecule). The intensity of emitted radiation depends on the concentration of the element in analyte. Comparing the emission intensity recorded with emission intensity of a reference standard the quantity of a given dopant can be determined in studied alloy.



Selected characteristic wavelengths for particular metals:

No	Element	nm
1	Co	237.853; 228.606; 231.145
2	Cu	224.709; 324.773
3	Fe	259.934; 273.944
4	Ni	231.595; 221.658
5	Pb	220.353; 217.005
6	Zn	213.867; 202.542
7	Al	309.27; 396.15
8	Sn	189.99

Experimental procedure:

Dissolving an alloy

1. Dissolve approximately 0.5 g alloy turnings in 20 ml HNO_3 by heating in baker on the burner (under hood). After complete reaction the solution should be heated until the nitrogen oxides removal, next evaporated to obtain dense solution (similar to syrup), and diluted to 100 ml and allow to stand.
2. If alloy contains tin dopant, precipitate of metastannic acid (H_2SnO_3) is formed.
3. After tin separation, add 5 ml H_2SO_4 (1:3) to the filtrate and evaporate to white fumes of SO_2 . Cool the solution and dilute it with water to 100 ml, carefully stirring with glass rod. If alloy contains lead dopant, PbSO_4 precipitate will settle. Filtrate it and perform identification reactions of Pb^{2+} ions.
4. If after PbSO_4 separation the filtrate is blue from Cu^{2+} ions, precipitate CuS using H_2S (under hood).
5. Filter off CuS precipitate. Remove hydrogen sulfide from the filtrate by boiling.

Classical qualitative analysis of metal dopants in alloy

In cool solution test the presence of two metals ions (indicated by the teachers) using known identification reactions, spot test analysis and microcrystalline analysis (exercises 2, 3, 4).

Semiquantitative determination of metal dopants in alloy using ICP-AES method

1. when solution (from point 1) is transparent (clear), transfer it quantitatively to volumetric flask (50 cm^3) and fill-up with distilled water to the mark

2. if the precipitate is present in the solution, filter it directly into the volumetric flask for 50 cm³ using filter paper (hard), wash the precipitate with several portions of H₂O and make-up with water to the mark

Attention:

If the solution in the flask (made-up to the mark) is not transparent, it should be centrifuged using plastic tubes.

The solutions prepared for microcomponent determination by ICP-AES method should be stored in plastic containers.

Perform the atomic emission spectra measurements using ICP-AES method for two metals (indicated by teachers) in the solution.

Prepare an report, describing the dissolving of alloy, classical qualitative identification and semiquantitative determination of metal dopants.