APPLICATION OF NEUTRON ACTIVATION ANALYSIS METHOD ON BIOMONITORS FOR ASSESSING ENVIRONMENT QUALITY

*E.A. NITESCU, S. VALECA, A.F. BUCSA**

University of Pitesti, Pitesti, Romania, alina_elena.nitescu@yahoo.com
**RATEN-ICN Pitesti, Mioveni, Romania, adrian.bucsa@nuclear.ro*

ABSTRACT

The purpose of this paper is to determine the chemical elements concentrations which affect both the population health and environment, such as toxic agents which are contained in air and are retained by precipitation inside the biomonitors vegetal tissues. The Neutron Activation Analysis is an analytic technique based on measuring the numbers and the energy of gamma radiation emitted by the radioactive isotopes produced in the sample matrix by irradiation with thermal neutrons in a nuclear reactor [1]. Usually, the samples are irradiated together with specific neutron flux monitors, duplicates and interest elements standards for a prior selected period of time inside the core of nuclear reactor. After the irradiation experiment and the specific radioactive decaying, can proceed measuring the gamma energies spectrum by using a high resolution detection system (HPGe – High Purity Germanium crystal) for gamma spectrometry and then assess the impact of the traced elements on population and environment.

Key words: Neutron Activation Analysis, biomonitor, HPGe

Introduction

In urban areas, air quality is strongly influenced by the many human activities. High population density, heavy traffic, domestic heating in winter and other industrial activities, are influencing concentrations of trace chemical dangerous elements in the atmosphere. Consequently, the population is exposed to potential adverse effects arising from changes in the composition of urban air. Thus, monitoring air quality has become one of the standard quality control procedures for assessing urban environment. The environment must be protected from pollutants to avoid its destruction and hence affecting the population in terms of health. What must be kept under control, especially nowadays, are massive heavy metal pollution from various industrial activity and beyond. For this reason we must have a fair and accurate assessment of these quantities of metals (how much is allowed to exist in the environment without affecting our health) and also qualitative assessment of these pollutants (what contains the air we breathe every day). There are many studies about atmospheric contamination but most of these have been limited because of the financial problems, i.e. high costs and the difficulty of carrying out extensive studies in terms of both time and space. To determine these dangerous chemical elements that adversely affect human health, we used an indicator namely moss plant as explained in references [2] and [3]. This plant has the ability to retain in the vegetative tissues precipitated chemical elements from the atmosphere because it lacks the cuticle that would stop the entry of elements within cells. Mosses were sampled and processed and the final form of dry residue obtained was introduced into polypropylene cartridges and then they were irradiated in the TRIGA ACPR rabbit. After the samples were activated in thermal neutron flux for a certain period of time, they were measured using a high resolution gamma-ray detection system

with crystal detector and an electronic system (preamplifier, pulsating unit, polarization module, amplifier) and a multichannel analyzer provided with a genuine specific software. These devices have led to the highest achievement of qualitative analysis of the sample (which chemical elements are contained in the sample) and quantitative analysis (concentration of the traced elements) using neutron activation analysis k0 standardization. The results can be used to achieve a graphical representation of areas with a high degree of pollution and based on it important decisions can be made to reduce the pollution.

Experimental

Analytical steps of Neutron Activation Analysis are as follows:

- ✓ Phase I of analysis: sample preparation means in most cases just grinding (pulverization), homogenization, mass determination, roasting, packaging and also selecting the best analytical process and preparation standards if any.
- ✓ Phase II of analysis: irradiating the samples. For irradiating the samples we used TRIGA ACPR facility which is a high efficiency neutron source for applying neutron activation analysis (a neutron flux in the range from 10^{12} to 10^{14} neutron $\cdot$ $cm^{-2} \cdot s^{-1}$).
- ✓ Phase III of analysis: measurement, evaluation and calculation considering gamma spectrum and the concentrations level of the trace elements. The most widely used gamma spectrometer consist of semiconductor detectors based on germanium connected to a computer using as a multi-channel analyzer for assessing and calculating the spectrum.

Phase I of analysis

For the experimental part of the research work we have taken a number of 4 samples from different locations of Pitesti city as shown in the *Table 1*:

Table 1. *Samples identification for irradiation experiment conducted in TRIGA ACPR Reactor*

Sample no.	Sampling location	Sample mass (g)	Sample ID
1	TRIGA Reactor stack	4470E-5	P1
2	Pitesti South Railway	6715E-5	P2
3	ARPECHIM Refinery	10884E-5	P3
4	ROLAST S.A. („GAVANA" area)	12113E-5	P4

After sampling, the mosses were stored in polyethylene bags at room temperature for 10 days after which they were weighed and then were placed in an oven at a temperature of 40° C. Measurements were performed regularly after which the mass was further dried in an oven until the weight of the mosses remained constant. The samples were then burned out in CTD 2-type oven at the temperature of 450° C until there was obtained a white ash. The reason of burning is to remove the water content from the vegetative tissue and because we need to have a homogenous composition of elements in the sample during irradiation experiment. *Figure 1* indicates the variation of masses for all samples from initial state to the ash state. For measuring the value of thermal neutron flux inside the irradiation location gold thin foil was used (aluminum diluted gold 0.1%). This monitor foil was washed with alcohol and then dried at 40^{o}C.

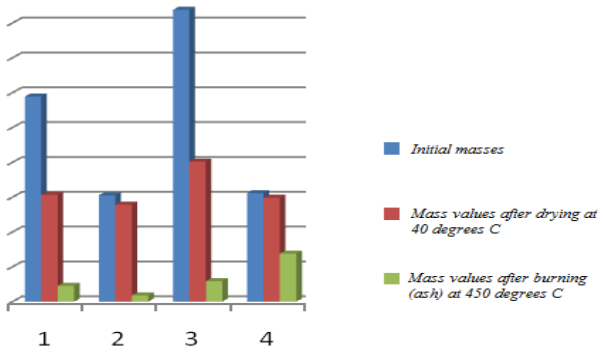

Fig. 1 *Mosses mass trend between sampling and burning (ready to be irradiated)*

Phase II of analysis

The samples were inserted in polyethylene cartridges after being weighted and then they were placed inside the TRIGA ACPR rabbit together with the gold foil monitor.

Table 2 shows the values for the reaction rates of the flux monitor reaction, [^{197}Au(n,γ)^{198}Au] and thermal neutron flux values indicated by the monitor (obtained from the calculations).

Table 2. *Thermal neutron flux measurements indicated by gold monitor inside the TRIGA ACPR rabbit (D-10 location of the core grid).*

Thermal neutron flux measurements in TRIGA ACPR rabbit (D-10) by gold monitor Au0,1%

Irradiation date	11/2/2016		
Start:	11:07:14		
Stop:	12:16:16	$T_{irradiation}$(sec)	4142
$P_{thermal}$ (MW)	63kW		
Monitor	Au0,1%	$\Phi_{monitor}$	4 mm
M(g)	4.59E-03		
σ_0 (cm^{-2})	9.88E-23		

No.	Tr(h)	R (dis/(nucl*s))	Rcd	Thermal flux (n/cm^2*s)	R(average) (dis/nuc/*s)	Dev std (n-1) (rate)	Average flux (n/cm^2*s)	Devstd (n-1) (flux)
1	23.55	1.7790E-10	2.10	9.432E+11				
2	28.58	1.8020E-10	2.10	9.554E+11				
3	53.58	1.7653E-10	2.10	9.359E+11				
4	67.66	1.7679E-10	2.10	9.373E+11				
5	145.83	1.7930E-10	2.10	9.506E+11	**1.7862E-10**	1.4677E-12	**9.470E+11**	7.78E+09
6	151.07	1.8030E-10	2.10	9.559E+11				
7	163.7	1.7830E-10	2.10	9.453E+11				
8	168.78	1.7960E-10	2.10	9.522E+11				

Calculations resulting from irradiation showed an average thermal neutron flux of 9.47*10^{11} neutrons*cm^{-2} * s^{-1}).

Phase III of analysis

It should be noted that the irradiation time was too short and so it did not permit to activate any of heavy metal elements. So in 4142 seconds irradiation it were successfully activated isotopes with short lifetime like: ^{55}Mn , ^{41}K , ^{45}Sc , ^{121}Sb , ^{139}La , ^{151}Eu , ^{75}As , ^{81}Br, ^{58}Fe. For every irradiated sample we conducted a set of 8 measurements for each.

Qualitative - quantitative measurements of the elements retained in the moss were done by using k0 standardization method of NAA. Accordingly to NAA k0-standardization method, one trace element concentration in a sample is obtained from the following equation detailed explained by reference [4] and [5]:

$$\rho_a(\mu g/g) = \frac{\left(\frac{N_p/t_c}{SDCW}\right)_a}{A_{sp,m}} \cdot \frac{1}{k_{0,m}(a)} \cdot \frac{G_{th,m}\cdot f + G_{e,m}\cdot Q_{0,m}(\alpha)}{G_{th,a}\cdot f + G_{e,a}\cdot Q_{0,a}(\alpha)} \cdot \frac{\varepsilon_{p,m}}{\varepsilon_{p,a}} \cdot 10^6$$

Where:

ρ_a - The concentration of the traced element "a" (μ g/ g);

m - Co-irradiated monitor for neutron fluency monitoring;

N_p - Net peak area measured and corrected by pulse losses (dead time, real coincidence);

t_c - measuring time [s];

S Saturation factor; = 1-exp(- $\lambda\, t_{irr}$), with t_{irr} – irradiation time and λ = (ln2)/$T_{1/2}$ with $T_{1/2}$ – halftime;

D Decay factor; = 1-exp(- $\lambda\, t_d$), where t_d – decay time (from the end of irradiation to the start of measurement);

C - Counting factor; = [1-exp(- $\lambda\, t_c$)]/ $\lambda\, t_c$, correction for decay during measurement;

W - Sample mass [g];

A_{sp} - = $(N_p/t_c)/SDCw$, specific counting rate, with w – monitor element mass [g];

$k_{0,m}(a)$ k_0 factor experimental calculated of the traced element "a" relative to "m" monitor, defined as:

$k_{0,m}(a) = (M_m\theta_a\sigma_{0,a}\gamma_a)/(M_a\theta_m\sigma_{0,m}\gamma_m)$, with M – molar mass,

θ – isotopic abundance, σ_0 – cross-section of (n,γ) reaction at 2200 m·s^{-1} and γ – absolute gamma-ray intensity;

G_{th} - thermal neutron self-shielding correction factor;

G_e - epithermal neutron self-shielding correction factor;

f - Φ_{th}/Φ_e , thermal to epithermal neutron ratio; (for ACPR reactor f factor value at the time of the experiment was 17.12);

$Q_0(\alpha)$ - = $(Q_0 - 0.429)\bar{E}_r^{-\alpha} + 0.429/(0.55)^{\alpha}(2\alpha+1)\,(1eV)^{\alpha}$, where $Q_0 = I_0/\sigma_0$, and I_0 represents the resonance integral defined as:

$$I_0 = \int_{0.55eV}^{\infty} \sigma(E)dE/E$$

$\bar{E}_r$ - Effective energy of the resonance expressed in eV;

α -value for the distribution deviation of the epithermal neutron compared with the ideal shape 1/E, approximated by a $1/E^{1+\alpha}$ dependency; (for ACPR reactor f factor value at the time of the experiment was 0.01159);

ε_p - Detection efficiency for full energy peak;

Results

The results of the Neutron Activation Analysis k0-standardization obtained after measuring all the samples on HPGe detector are presented in the *Figures 2 – 10.*

Bromine

Long-term use of potassium bromide (or any of the salts of bromine) may lead to bromism. This state of central nervous system depression is caused by bromide moderate doses on the order of several grams to humans or other mammals. Ingesting bromine can also cause a rash on the skin similar to acne.

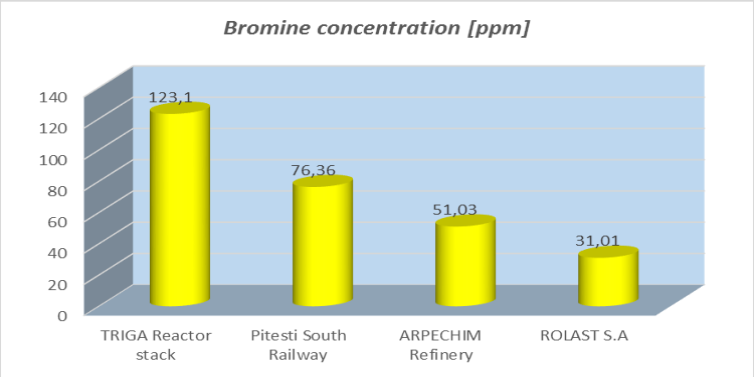

Fig. 2. *Bromine concentration in the samples*

Antimony

Antimony and many of its campounds are toxic and effects of antimony poisoning are similar to arsenic poisoning. Inhalation of antimony dust is very harmful and in some cases can be fatal; in small doses, antimony causes headache, dizziness and depression. Higher doses and prolonged skin contact may cause dermatitis; it can also cause liver and kidney damaga, causing violent vomiting and lead to death within days

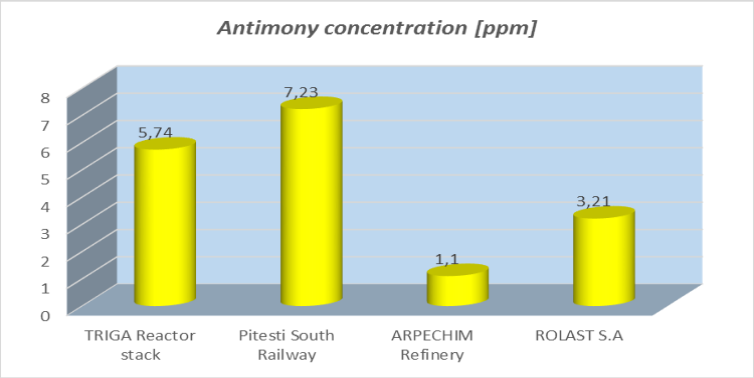

Fig. 3. *Antimony concentration in the samples*

Arsenic

Arsenic and many of its compounds are generally very strong poisons. Many water sources near mines are contaminated with these poisons. European Union under Directive 67/548/EEC of International Agency for Research on Cancer recognizes arsenic and its compounds as being in the first group of carcinogens. Arsenic is responsible for the most cases of poisoning of all heavy metal. Arsenic is released into the environment through the process of smelting copper, zinc and lead as well as by producing chemicals or bottles. "Arsine" gas is a by-product that occurs following the occurrence of pesticides that contain arsenic. Arsenic can be found in water sources all over the world, involving crustaceans and fishes exposure. Other sources are paints, poisons for rats, fungicides and inhibitory substances of wood aging. Target organs are the blood, kidneys, central nervous system, digestive tract and skin.

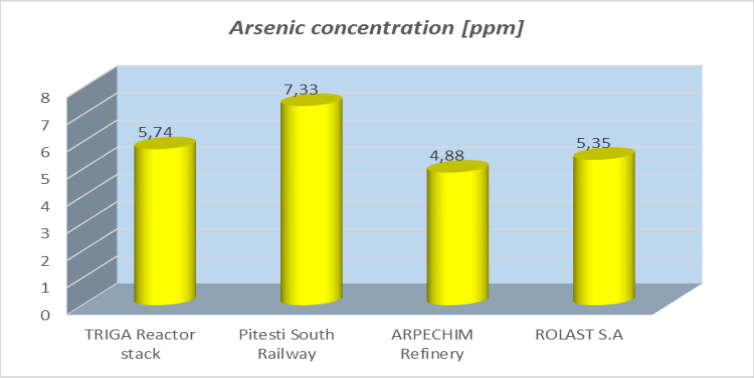

Fig. 4. *Arsenic concentration in the samples*

Europium

There are clear indications that europium is in particular less toxic compared to other heavy metals. Europium dust presents a danger of fire (flammable) and explosion. Variation is represented in the following figure.

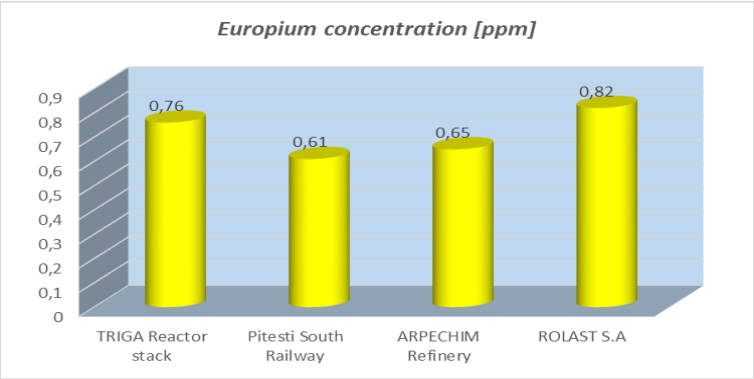

Fig. 5. *Europium concentration in the samples*

Scandium

Elemental scandium is considered non-toxic element. Average lethal dose for scandium chloride (III) for guinea pigs was determined at a value of 4 mg/kg for the inter-stomach area and 755 mg/kg for oral administration. In the light of these results, scandium compounds must be treated as having moderate toxicity.

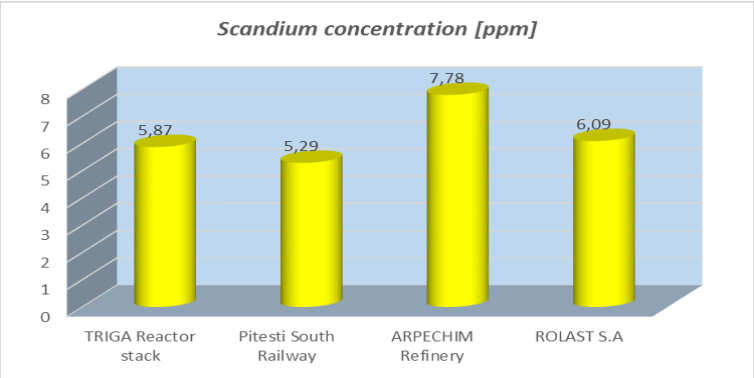

Fig. 6. *Scandium concentration in the samples*

Potassium

Because of the powerful reactive nature of potassium, it must be handled with care, with skin and eye protection and preferably an explosion-resistant barrier between the user and metal. Ingesting large quantities of potassium can lead to hyperkalemia strongly influencing the cardiovascular system.

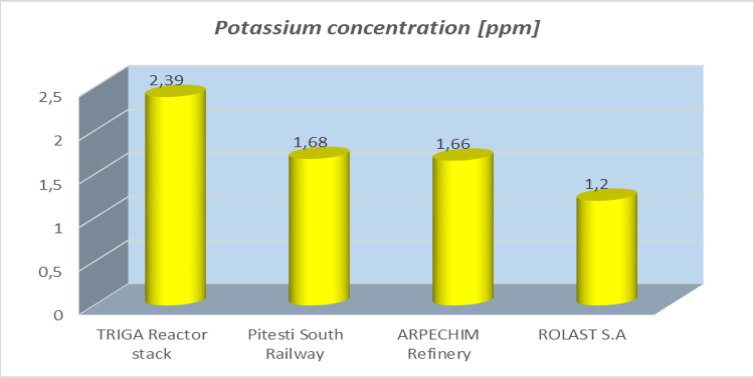

Fig. 7. *Potassium concentration in the samples*

Iron

This heavy metal is of major importance, especially because of the iron based supplements in the diet that can poison young children acutely. Ingestion is the main way that the iron enters the body exposing the toxic effects because iron is rapidly absorbed in the gastrointestinal tract. Corrosive nature seems to increase the absorption of iron. Most overdoses are the result of wrong ferrous sulphate tablets ingestion by children because they are covered in red capsule or by adults on basic multivitamin preparations. Other sources of iron include drinking water, iron pipes and cooking vessels. Target organs are the liver, kidneys and cardiovascular system. Large amounts of ingested iron can cause excessive increase iron levels in the blood. High levels of free iron in the blood reacts with peroxides and produce free radicals, which are highly reactive and can attack DNA, proteins, lipids and other cellular compounds. Iron usually affects heart cells, liver and is causing adverse effects including coma, metabolic acidosis, shock, impaired liver functions, coagulopathy, long-term organ damage and even death. A dose of 20 mg and 60 mg of iron per kg mass is considered to be lethal.

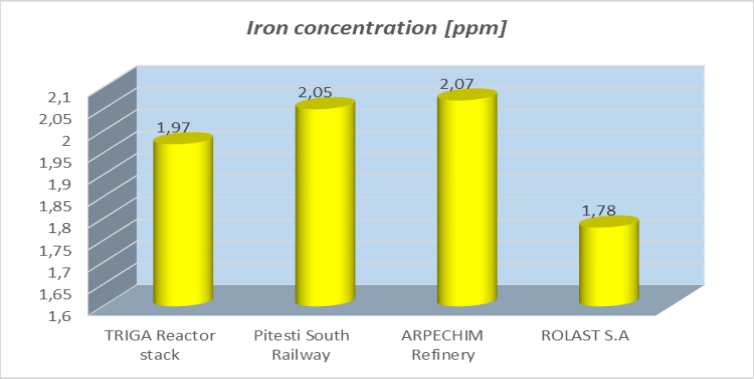

Fig. 8. *Iron concentration in the samples*

Manganese

Manganese compounds are less toxic than other metal such as nickel and copper. However, manganese dust exposure limit value should not exceed 5 mg/m^3 even for small periods of time because of its toxicity level. Manganese poisoning was coupled with disturbances in the body and locomotor function and with cognitive disorders. Manganese exposure among miners was associated with a from of neurodegeneration similar to Parkinson's disease called " manganism" . High levels of exposure to manganese in drinking water have been associated with impaired intellectual and reducing the coefficient of intelligence at school children. Manganism occurs in people engaged in the production or processing of manganese alloys, in workers exposed to manganese and fungicides. In general, concentrations of manganese in the environment more that 5 mg Mn/m^3 can cause specific symptoms.

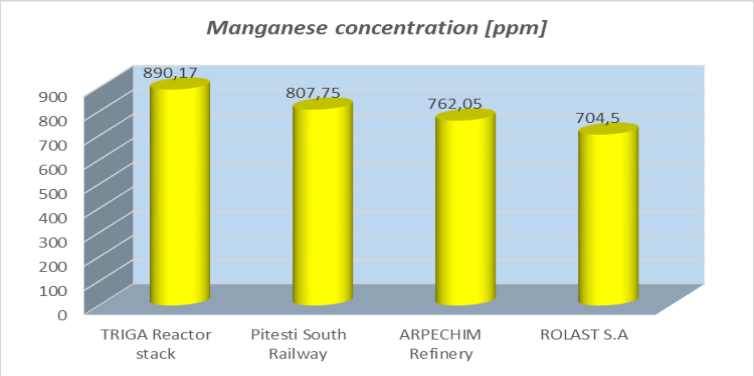

Fig. 9. *Manganese concentration in the samples*

Lanthanum

Lanthanum has a moderate level of toxicity and should be handled with care. Lanthanum produce hyperglycemia, lowers blood pressure, degeneration of the spleen and liver functions alteration.

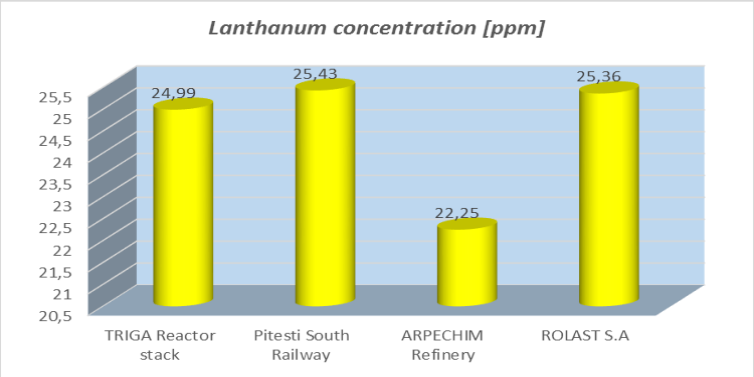

Fig. 10. *Lanthanum concentration in the samples*

Conclusion

The NAA-k0 method allows to trace a wide range of chemical elements which can be activated in a nuclear reactor. Solid and liquid samples can be studied with this method. The characterization of the biomonitors samples made in this paper represents a detailed work which can help to draw a map of the most polluted area from the Pitesti city. These results can also help in taking actions of prevent future development of industrial activities in these areas to avoid the increasing of pollution and by this affecting the humans and environment as well.

Acknowledgements

Special thanks to NAA personnel from TRIGA Reactor from ICN PITESTI for all the support brought in this experimental work.

References

[1] Zs. Molnár – "Neutron Activation Analysis".
[2] D. Popovic – "Trace elements and radionuclides in urban air monitored by moss and tree leaves".
[3] G. Kirchner – "The potential of lichens as long-term biomonitors of natural and artificial radionuclides".
[4] F. DeCorte – "The K_0 standardization method".
[5] F. DeCorte & A. Simonits – "Vade mecum for K_0-users".