# 1.27 APPLICATION FOR AIRBORNE PARTICULATE MATTER AS A DEMONSTRATION USING $k_0$-NAA METHOD IN DALAT NUCLEAR RESEARCH INSTITUTE OF VIETNAM

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## ABSTRACT

The airborne particulate samples have been collected using two types of polycarbonate membrane filter $PM_{2.5}$ and $PM_{2.5-10}$ in two typical sites of industrial (Ho Chi Minh City) and rural (Dateh) regions in south of Vietnam. The concentration of trace elements in the samples has been determined by the $k_0$-NAA procedure developed in Dalat NRI. In order to check the developed $k_0$-NAA procedure for the airborne particulate matter, two standard reference materials (SRMs) Urban Particulate NIST-1648 and Vehicle Exhaust Particulates NIES-8 were analyzed and the obtained results have been compared and interpreted in term of deviation between experimental results and the certified values.

## INTRODUCTION

In the research programme on monitoring of air pollution in Vietnam, some sites have been selected to collect the airborne particulate samples using two types of polycarbonate membrane filter $PM_{2.5}$ and $PM_{2.5-10}$. The airborne particulate samples collected from two sites of industrial (Ho Chi Minh City) and rural (Dateh) regions in south of Vietnam have been analyzed. The number of interested elements in the airborne particulate matter are large of about 30, so when using the conventional relative NAA method the number of used SRMs must be more than one (about three). This leds to the systematical error of the analytical results depend on the different SRMs affecting to the result interpretation.

The $k_0$-NAA is a technique capable of multielemental analysis, relatively simple to carry out and in particular for that systematical error is stable. The $k_0$-NAA method allows the concentration determination of all elements of which activated radionuclides can be quantified by γ-ray spectrometry, even if this element determination was not foreseen (for instance, in the case of a sample contamination).

This report briefly describes the application of the $k_0$-NAA method for airborne particulate matter in order to show an overtop advantage of the $k_0$-NAA method for this object.

## EXPERIMENTAL

*Sampling and sample preparation*

Sampling sites: Industrial (Ho Chi Minh City) and rural (Dateh) regions

Sampling period: January – October 2002

Sampling frequency: Each week

Sampling time: 24 h (flow rate: 18 lpm)

Coarse fraction: $PM_{2.5-10}$ and Fine fraction: $<PM_{2.5}$

Filter: Polycarbonate membrane filter 47 mm diameter, 8 μm and 4 μm pore size

Weighing: Maintain the same condition before and after sampling.

Sampling address: (1) Dateh District, Lamdong Province (Vietnam), latitude: 11°31' N, longitude: 107°28' E, altitude: 800 m; (2) Truong Dinh Street, 1st District, Ho Chi Minh City (Vietnam), latitude: 10°46' N, longitude: 106°41' E, altitude: 9 m.

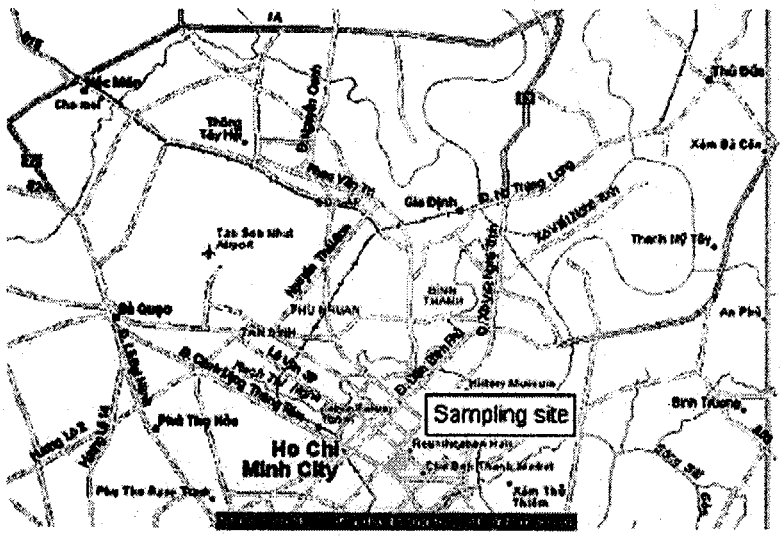


**Fig 1.** The rough map of Ho Chi Minh City site

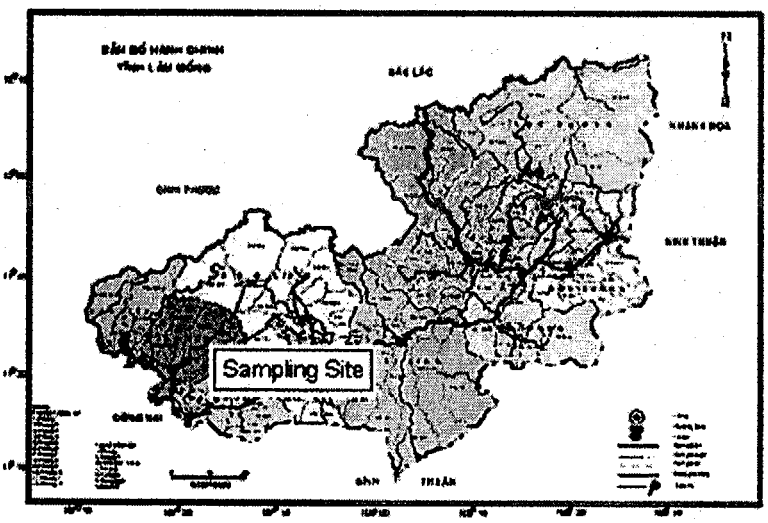


**Fig 2.** The rough map of Dateh site

The samples (filters containing airborne particulate matter) were folded so that they can put into 1cm × 1cm polyethylene vials and then sealed by heating. Before measurement, the samples have been transferred to new vials. Themselves of the short irradiated samples were used repetitively for the long irradiation.

The monitors used were sheet of Zr (99.8%, thickness 0.125 mm, ADVENT Research Materials Ltd.), wires of Al-0.11%Au (dia. 0.5 mm, IRMM) and Ni (99.98%, dia. 0.076 mm for determination of fast neutron).

*The $k_0$-NAA procedure*

Neutron source: Dalat research reactor of 500 kW power.

Irradiation facilities: Dry channel 7-1 using pneumatic transfer system for short irradiation down to 45 seconds and 40 wet irradiation holes in rotary rack using manual for long irradiation up to 20 hours.

Thermal neutron flux: $4.6 \times 10^{12}$ n/cm$^2$.sec and $3.5 \times 10^{12}$ n/cm$^2$.sec for channel 7-1 and rotary rack, respectively.

Counting system: Ortec GMX-30190 detector using automatic sample changer model ASC2 possibly for 40 samples in a measurement batch, and a Canberra GX1520 detector using manual. Acquisition and analysis software using Ortec GammaVision 5.32 for both gamma-ray spectrometers connected to an Ortec 919E MCB.

Data processing: The "Ko-DALAT" software developed in NRI.

Quality control: Urban Particulate NIST-1648 and Vehicle Exhaust Particulates NIES-8. Data intercomparison work has been participated by IAEA.

The irradiation, decay and counting time parameters for the airborne particulate sam ples are showed in Table 1.

**Table 1.** Irradiation, decay and counting time for the airborne particulate samples

| | **Irradiation time** | **Decay time** | **Counting time** | **Nuclides** |
|---|---|---|---|---|
| Short | 5 m | 5 m | 300 s | Al, Ca, Cu, Mg, Ti, V |
| (Channel 7-1) | | 30 m | 900 s | Ba, Cl, I, In, K, Mn, Na |
| Long | 10 h | 2-3 d | 1800 s | Au, Br, La, $^{122}$Sb, Sm |
| (Rotary rack) | | 3 w | 7200 s | As, Au, Ce, Co, Cr, Cs, Fe, Hf, Lu, Rb, $^{124}$Sb, Sc, Se, Th, Yb, Zn |

The measurements are performed on the calibrated γ-ray spectrometers at the positions where the dead time of system is controlled as less than 5%.

*Calculation of concentrations and detection limits*

The concentration ρ of the element x in the sample is calculated from the following equation[1]:

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

where,

$m$ - coirradiated neutron fluence rate monitor;

$W$ - sample mass (in grams);

$k_{0,m}(a)$ - $k_0$-factor, $= \frac{M_m \gamma_a \theta_a \sigma_{0,a}}{M_a \gamma_m \theta_m \sigma_{0,m}}$ of analyte $a$ vs. monitor $m$;

$f$ $= \Phi_{th}/\Phi_e$ ratio;

$Q_0(\alpha)$ $= \frac{Q_0 - 0.429}{\overline{E}_r^{\alpha}} + \frac{0.429}{E_{Cd}^{\alpha}(2\alpha+1)}(1eV)^{\alpha}$, where $Q_0 = \frac{I_0}{\sigma_0}$, with

$I_0$ is the resonance integral, $E_{Cd}$ is the cadmium cut-off energy ($E_{Cd}$ = 0.55eV);

$\overline{E}_r$ - effective resonance energy in eV;

$\alpha$ - expression for the deviation of the epithermal neutron distribution from $1/E$ shape, approximated by a $1/E^{1+\alpha}$ dependence.

The calculation of detection limits is done in the same way. For a peak not found, the detection limit for the corresponding element can be calculated by replacing the term $N_p$ in the expression for concentration calculation with the detection limit in counts, according to Currie: $DL\ (counts) = 2.706 + 4.653\sqrt{B}$. Where, $B$ is the background counts at the expected peak energy. Peak width is taken equal to 3 times the detector resolution at this energy.

All these nuclear parameters such as $k_0$, $Q_0$, $\overline{E}_r$, and decay data have been introduced in the PC nuclear data library[2] integrated in the "Ko-DALAT" software in order to perform a fully automatic $k_0$-NAA treatment.

*Sources of error*

- Sample preparation: We carried out the tests with the aim of evaluating the mass imprecision and the possible losses during the sample preparation. The error calculated from the results is under 1.5%.

- Measurement conditions: The sample shape is well defined and the sample position with regard to the detector is defined better than 0.5 mm. The errors due to the sample position during the measurement are generally about 1 to 2%.
- Efficiency curve: The efficiency curve was established for the counting positions, using the γ-ray point sources ($^{241}$Am, $^{133}$Ba, $^{109}$Cd, $^{60}$Co, $^{137}$Cs and $^{152}$Eu) and the multinuclide standard source including $^{241}$Am, $^{133}$Ba, $^{109}$Cd, $^{139}$Ce, $^{57}$Co, $^{60}$Co, $^{137}$Cs, $^{203}$Hg, $^{113}$Sn, $^{85}$Sr and $^{88}$Y from Isotope Products Laboratories (USA). These errors are of the order of 1 to 2% for energies over 200 keV and of 3 to 5% for energies around 100 keV region.
- Nuclear data: The errors is evaluated for $k_0$ and $Q_0$ factors of about 1% [1].
- Flux monitor: The error has been estimated at 1.5% for α and 1% for $f$ [1].
- Time: The experimental conditions of this work, the error of time is negligible for long irradiation, but for short irradiation is estimated of about 1 to 2%.

The most important error occurs in the γ-ray spectrum processing of the net peak area determination, which depends on the counting statistic and the spectral matrix. As a consequence, the irradiation, decay and counting times should be optimized for each element group as showed in Table 1.

## RESULTS AND DISCUSSION

About 27 elements in the airborne particulate samples were determined. Tables 2 & 3 show mean concentration of trace elements in airborne particulate samples collected fro m two sites of Dateh and Ho Chi Minh City, respectively.

**Table 2.** Mean concentration of trace elements in Dateh region for fine and course fractions (unit ng/m$^3$).

| Elements | Samples | Coarse | | Fine | |
|---|---|---|---|---|---|
| | | Mean | STD | Mean | STD |
| Al | 35 | 1003 | 350 | 203 | 120 |
| As | 35 | 3.7 | 1.1 | 2.1 | 1.4 |
| Br | 40 | 13.4 | 1.9 | 5.5 | 0.9 |
| Ca | 40 | 752 | 140 | 523 | 120 |
| Ce | 35 | 4.2 | 1.3 | 3.4 | 1.2 |
| Cl | 35 | 1238 | 305 | 985 | 230 |
| Co | 35 | 0.65 | 0.31 | 0.58 | 0.23 |
| Cr | 40 | 4.76 | 1.52 | 4.23 | 1.35 |
| Cs | 40 | 0.35 | 0.14 | 0.30 | 0.12 |
| Cu | 35 | 156 | 22 | 59 | 18 |
| Fe | 40 | 1120 | 410 | 740 | 240 |
| Hf | 40 | 0.14 | 0.06 | 0.11 | 0.05 |
| K | 40 | 920 | 310 | 771 | 320 |
| La | 40 | 1.40 | 0.55 | 1.30 | 0.45 |
| Mg | 40 | 352 | 85 | 235 | 75 |
| Mn | 40 | 24.1 | 4.3 | 15.2 | 3.6 |
| Mo | 35 | 1.32 | 0.31 | 1.01 | 0.27 |
| Na | 40 | 430 | 75 | 230 | 67 |
| Rb | 35 | 3.1 | 0.9 | 2.3 | 0.7 |
| Sb | 40 | 11.9 | 1.7 | 5.6 | 1.4 |
| Sc | 40 | 0.3 | 0.1 | 0.2 | 0.1 |
| Se | 35 | 2.1 | 0.4 | 1.1 | 0.4 |
| Sm | 40 | 0.2 | 0.1 | 0.2 | 0.1 |
| Th | 40 | 0.35 | 0.14 | 0.31 | 0.11 |
| Ti | 40 | 87.2 | 16.5 | 65.7 | 12.6 |
| V | 40 | 3.6 | 0.8 | 2.1 | 0.7 |
| Zn | 40 | 102 | 22 | 75 | 11 |

**Table 3.** Mean concentration of trace elements in Ho Chi Minh region for fine and course fractions (unit ng/m$^3$).

| Elements | Samples | Coarse | | Fine | |
|---|---|---|---|---|---|
| | | Mean | STD | Mean | STD |
| Al | 35 | 1957 | 460 | 1756 | 360 |
| As | 30 | 5.7 | 1.9 | 4.1 | 1.7 |
| Ba | 30 | 56.2 | 2.7 | 32.1 | 2.2 |
| Br | 35 | 30.2 | 6.1 | 25.8 | 3.9 |
| Ca | 35 | 956 | 180 | 755 | 215 |
| Ce | 30 | 5.4 | 1.5 | 4.6 | 1.4 |
| Cl | 30 | 1751 | 324 | 1520 | 305 |
| Co | 30 | 0.72 | 0.35 | 0.66 | 0.21 |
| Cr | 35 | 6.02 | 1.89 | 5.22 | 1.41 |
| Cs | 35 | 0.45 | 0.16 | 0.40 | 0.13 |
| Cu | 30 | 278 | 24 | 215 | 21 |
| Fe | 35 | 1644 | 330 | 1350 | 116 |
| Hf | 35 | 0.3 | 0.1 | 0.2 | 0.1 |
| K | 35 | 1211 | 135 | 1144 | 120 |
| La | 35 | 2.1 | 0.7 | 1.5 | 0.4 |
| Mg | 35 | 542 | 57 | 329 | 67 |
| Mn | 35 | 41.7 | 4.2 | 37.1 | 3.6 |
| Mo | 30 | 1.42 | 0.10 | 1.21 | 0.09 |
| Na | 35 | 944 | 85 | 785 | 63 |
| Rb | 30 | 6.1 | 0.9 | 5.3 | 0.7 |
| Sb | 35 | 19.4 | 1.8 | 15.2 | 1.5 |
| Sc | 35 | 0.5 | 0.2 | 0.4 | 0.1 |
| Se | 30 | 3.2 | 0.5 | 2.7 | 0.3 |
| Sm | 35 | 0.4 | 0.1 | 0.3 | 0.1 |
| Th | 35 | 0.51 | 0.16 | 0.45 | 0.13 |
| Ti | 35 | 126.7 | 14.3 | 108.4 | 11.2 |
| V | 35 | 6.8 | 0.9 | 5.2 | 0.8 |
| Zn | 35 | 121 | 20 | 104 | 13 |

The SRMs Urban Particulate NIST-1648 and Vehicle Exhaust Particulates NIES-8 have been used to check for the developed $k_0$-NAA procedure.

Figures 3 and 4 show a comparison of experimental results and the certified values. The Z-scores are showed as error bars for each point on the chart.

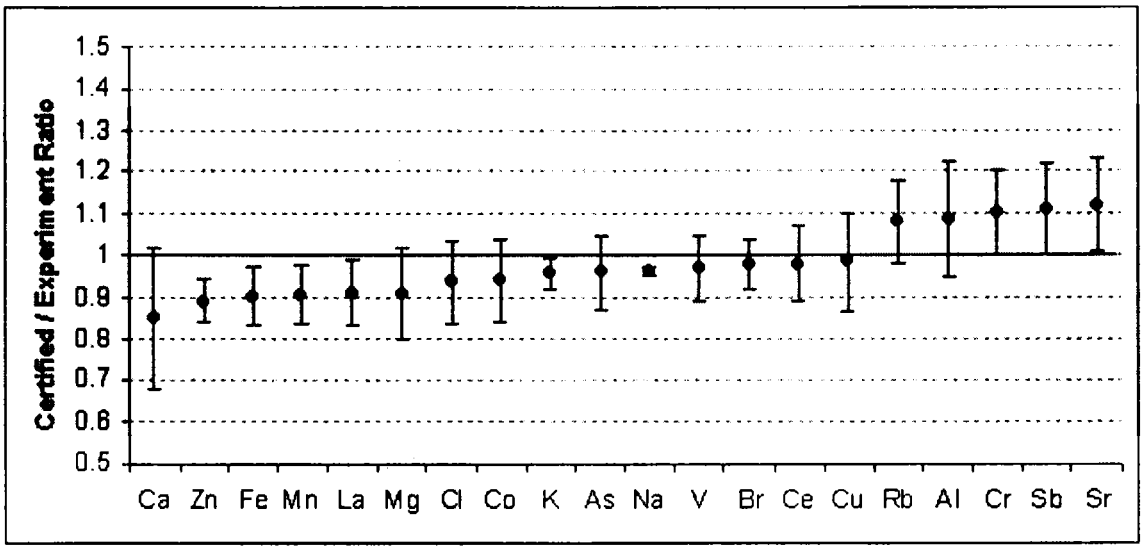


**Fig 3.** Comparison of experimental results and the certified values (NIST-1648)

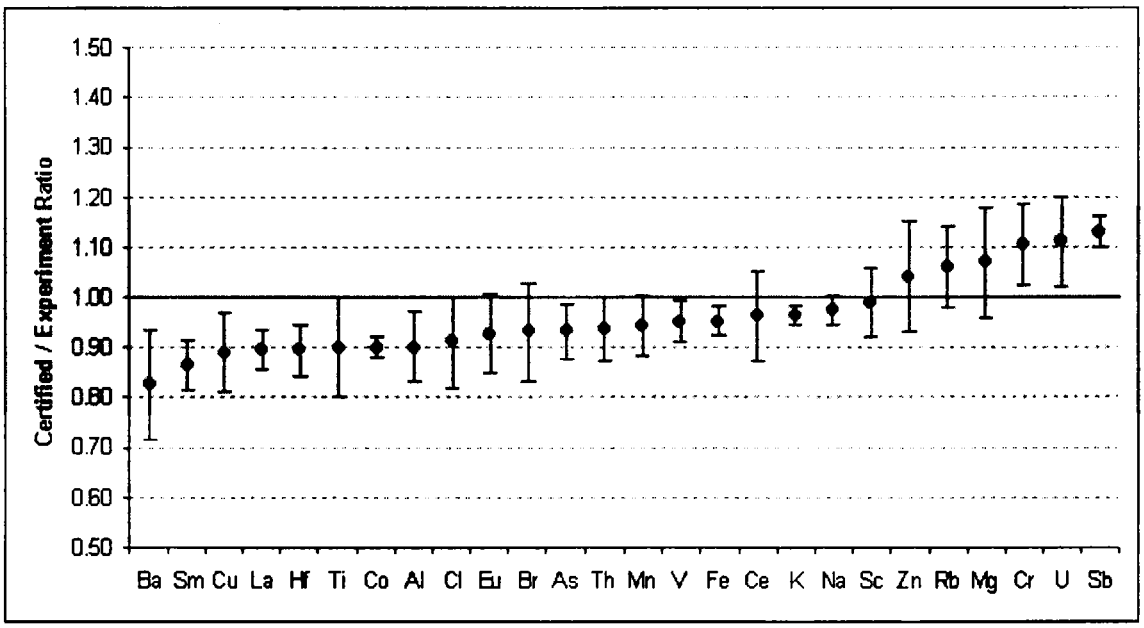


**Fig 4.** Comparison of experimental results and the certified values (NIES-8)

## CONCLUSIONS

A multi-element analysis procedure based on the $k_0$-NAA method allowing to simultaneously determine concentrations for about 27 elements (Al, As, Ba, Br, Ca, Ce, C l, Co, Cr, Cu, Fe, Hf, K, La, Mg, Mn, Na, Rb, Sb, Sc, Sm, Sr, Th, Ti, U, V, and Zn) in airb orne particulate matter collected using the polycarbonate membrane filters, was developed at the Dalat research reactor.

The obtained results have revealed that the $k_0$-NAA procedure enables an absolute direct analysis, avoiding the use of a lot of standards and thus simplifies the preparation for analysis.

The application of $k_0$-NAA procedure can be generally applied for to the characterization of airborne particulate matter, which are difficult to find the proper reference materials and therefore regarded as a successful application of the method.

## ACKNOWLEDGEMENTS

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## REFERENCES

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