

## Application of nuclear techniques to study of trace elements

A S DIVATIA

Nuclear Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India

**Abstract.** Trace elements in various materials using nuclear techniques are studied. Results obtained by using energy-dispersive X-ray fluorescence (EDXRF) and proton-induced X-ray emission (PIXE) are examined. The EDXRF method is used to quantitatively evaluate trace elements such as Mn, Fe, Cu, Zn, Br, Rb and Sr in tea leaves. Correlation of trace elements in tea leaves and in the corresponding soil is studied.

**Keywords.** Nuclear techniques; trace elements; energy-dispersive X-ray fluorescence (EDXRF); proton-induced X-ray emission.

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### 1. Introduction

Over the last fifty years nuclear physics has progressed exponentially, probing deeper and deeper into the nucleus; we are now at the stage of quarks and gluons. This phenomenal progress has been accompanied by an equally phenomenal progress in nuclear techniques which have found important applications in a variety of fields.

Study of trace elements in various materials using nuclear techniques provides valuable information in many fields. Trace elements can be determined generally to ppm quantities and in special cases to ppb quantities.

### 2. Nuclear techniques

The following nuclear techniques are useful for elemental analysis: (i) activation analysis; (ii) nuclear scattering; (iii) nuclear reactions; (iv) energy-dispersive X-ray fluorescence (EDXRF); and (v) proton-induced X-ray emission (PIXE). During bombardment of a sample material by an ion beam, nuclear reaction or nuclear scattering takes place and  $\gamma$ -rays, protons, deuterons, alphas etc or neutrons are emitted, leaving either a stable or an unstable nucleus. The outgoing particles or  $\gamma$ -rays can be detected by appropriate nuclear detectors. In nuclear scattering, recoil energies of  $^4\text{He}$  ions as a function of scattering angle are different for different elements. It can be shown that good elemental separation can be achieved particularly at backward angles.

For example, elemental analysis of two different varieties of glass (soda glass and pyrex glass) using  $(\alpha, p)$  reaction clearly reveals the difference between the two glasses, since proton peaks from  $^{23}\text{Na}(\alpha, p)$  reactions are prominent in soda glass and those from  $^{11}\text{B}(\alpha, p)$  reactions are prominent in pyrex glass. Another example is the  $^{19}\text{F}(p, \alpha\gamma)^{16}\text{O}$  reaction, which has been used (Chaudhri *et al* 1975) to determine the

flourine content in tea, by obtaining a  $\gamma$  spectrum from a thick target of Darjeeling tea under bombardment with 5 MeV protons. Prominent  $\gamma$ -peaks from the reaction indicate the presence of flourine in tea.

### 3. EDXRF and PIXE

One of the most elegant methods used for trace element analysis in materials is by X-ray fluorescence. The EDXRF method gives multielement analysis of trace elements without destroying the sample. Figure 1 shows two possible experimental arrangements for EDXRF analysis.  $\gamma$ -rays from a radioactive source produce X-ray fluorescence. Low energy X-rays are detected by a Si(Li) detector and the complete spectrum is processed by a multichannel analyser, a display unit and an on-line computer. An X-ray tube can also be used. When protons are used for excitation, PIXE takes place. A list of the useful radioisotopes for XRF work is shown in table 1. In general, the collimated side source geometry is more sensitive. X-ray line intensity is expressed as

$$yI_j = I_0 GK_j m_j c_j,$$

where  $I_0$  is the intensity of exciting source and  $G$ , the geometrical factor.  $K_j$ , the relative excitation-cum-detection factor is expressed as

$$\tau(1 - 1/J_{KL})\omega_{KL}fT\varepsilon$$

where  $\tau$  is the total photoelectric cross-section,  $J_{KL}$  is the jump ratio for  $K$  or  $L$  absorption edge,  $\omega_{KL}$ , the fluorescence yield,  $f$ , the intensity/total intensity  $K$  or  $L$ ,  $T$ , the fraction of X-rays transmitted and  $\varepsilon$ , the detector efficiency. In the above expression  $m_j$  is the concentration of element and  $c_j$  the absorption factor is given as

$$\frac{1 - [\exp]^{- (\mu_1 \operatorname{cosec} \theta_1 + \mu_2 \operatorname{cosec} \theta_2) \cdot m}}{(\mu_1 \operatorname{cosec} \theta_1 + \mu_2 \operatorname{cosec} \theta_2) \cdot m},$$

$\mu_1, \mu_2$  are the total mass absorption coefficient for exciting and characteristic X-ray,  $\theta_1, \theta_2$  are the angles formed by exciting rays and elemental X-rays and  $m$  is the mass of sample (in  $\text{g}/\text{cm}^2$ ).

Table 1. Some useful isotopes for EDXRF work.

Isotope	Half-life	Photon emission (keV)	Useful range
$^{55}\text{Fe}$	27y	5.9 (Mn $K_\alpha$ ) 6.5 (Mn $K_\beta$ )	$^{13}\text{Al}$ - $^{24}\text{Cr}$
$^{109}\text{Cd}$	453d	22.2 (Ag $K_\alpha$ ) 25 (Ag $K_\beta$ ) 88 (I.T. 3.7%)	$K$ - $^{22}\text{Ti}$ - $^{44}\text{Ru}$ $L$ - $^{73}\text{Ta}$ - $^{92}\text{U}$ $^{56}\text{Ba}$ - $^{82}\text{Pb}$
$^{238}\text{Pu}$	92y	40 ( $\gamma$ )	$^{28}\text{Ni}$ - $^{56}\text{Ba}$
$^{241}\text{Am}$	433y	59.6 ( $\gamma$ )	$K$ - $^{26}\text{Fe}$ - $^{69}\text{Tm}$ $L$ - $^{73}\text{Ta}$ - $^{92}\text{U}$

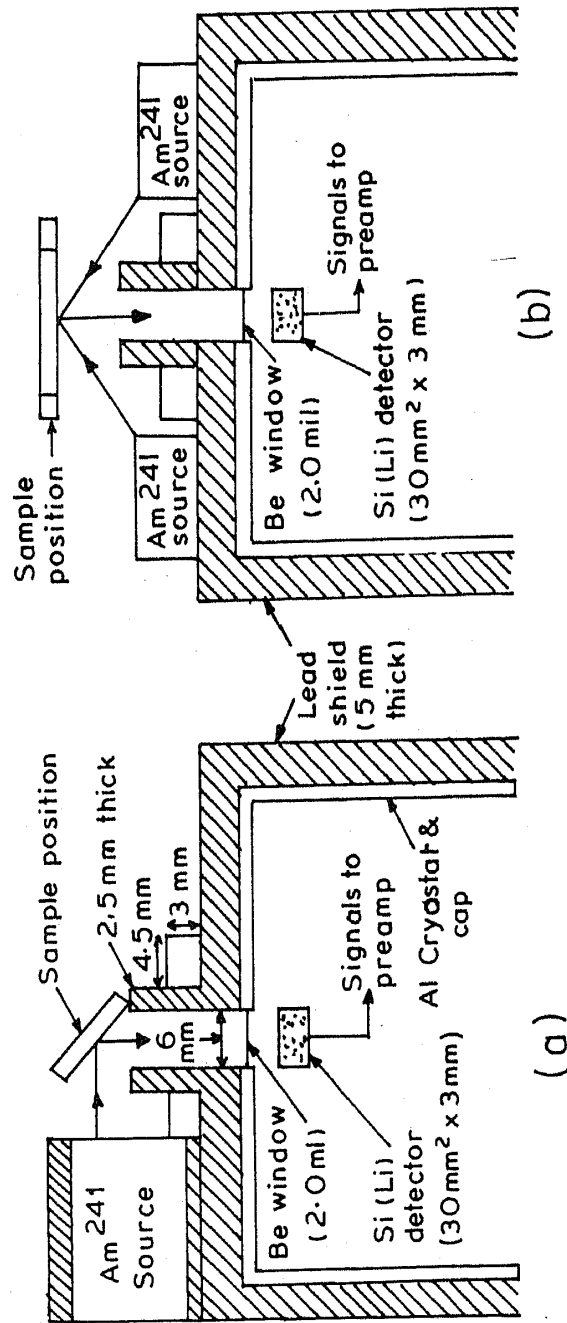


Figure 1. Schematic arrangements of (a) side source geometry and (b) annular source geometry.

Further, the Compton scattered intensity is given as

$$I_{sc} = I_0 GK \sigma_{sc} C_{sc} m,$$

where  $\sigma_{sc}$  is the total scattering cross-section of the sample,  $C_{sc}$ , the self-absorption factor for source and scattered radiation and  $K$ , the detection factor for scattered radiation. Hence,

$$I_j/I_{sc} = K_j/K \sigma_{sc} \cdot m_j/m \cdot C_j/C_{sc},$$

where  $C_j/C_{sc}$  is obtained by a transmission method experiment and the calibration is done by a standard source.

For trace element determination EDXRF and PIXE methods are not equally effective in the case of all elements. Their effectiveness can be seen in figures 2 and 3, where minimum detection limits are shown with EDXRF and PIXE respectively for different elements.

#### 4. Trace element studies in materials

Some universities and institutions in India have undertaken study of trace elements in materials of relevance and it is of interest to consider the results obtained. Sudhir Kumar *et al* (1986) studied air and water samples using the EDXRF technique, and obtained X-ray spectra of ground water and air particulate.

Sawhney *et al* (1986), carried out Dal Lake sediment studies using EDXRF spectrometry. A representative spectrum of the sediment is shown in figure 4. Mehta (1986) studied proton-induced X-ray emission. Figure 5 shows a multielement analysis of trace elements in water from a stream in Meghalaya obtained by Choudhury *et al* (1986).

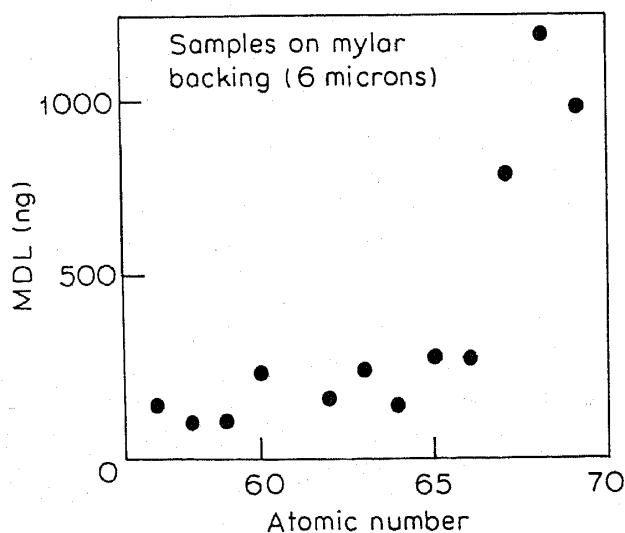


Figure 2. Minimum detection limits obtained for elements  $57 \leq Z \leq 69$  for mylar based thin samples in the optimum geometry.

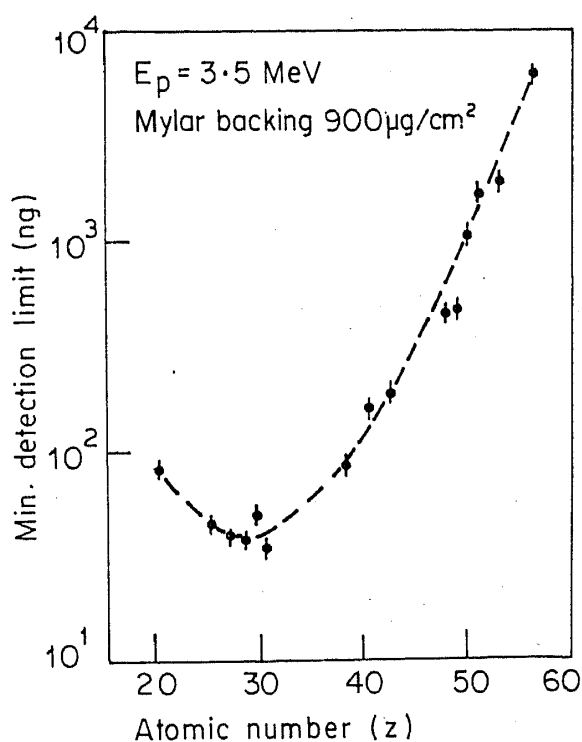


Figure 3. Minimum detection limits obtained for different elements by excitation with proton beam.

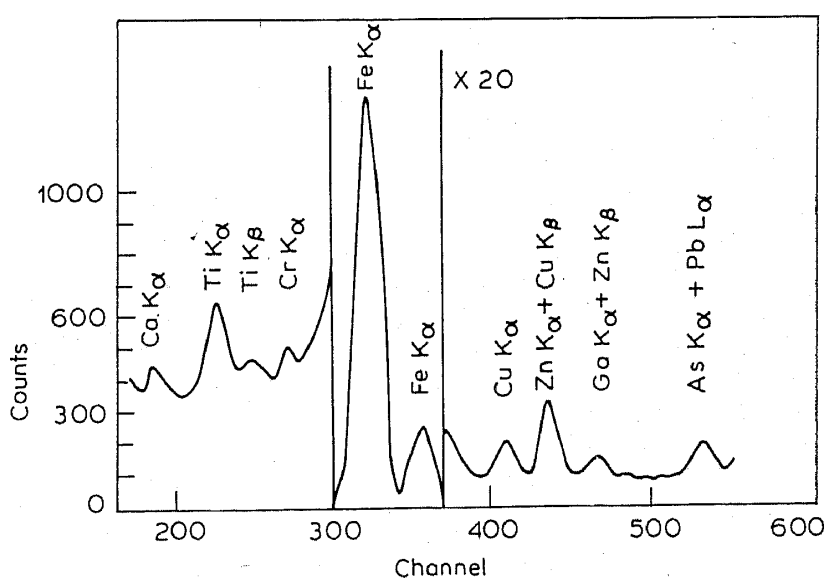


Figure 4. Representative EDXRF spectrum of the Dal Lake sediment with  $^{238}\text{Pu}$  excitation source.

### 5. Trace element studies in tea

In view of the usefulness of EDXRF and PIXE techniques and the importance of tea in India's economy, it was decided to carry out trace element studies in tea at the Nuclear Physics Division, BARC. The tea plant, 'Thea sinensis' or 'camellia sinensis'

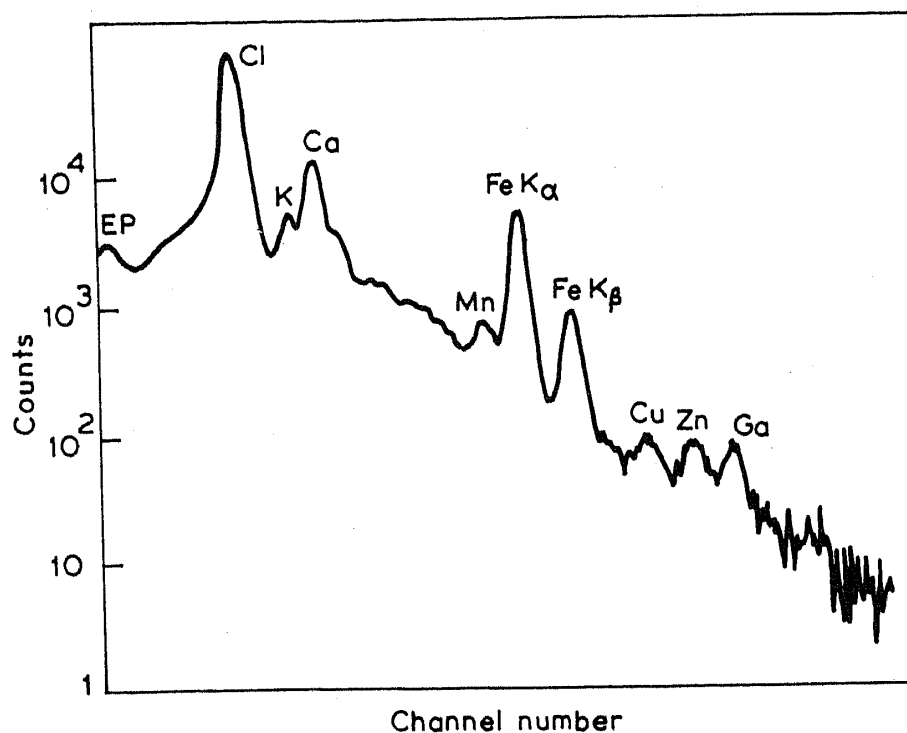


Figure 5. Typical PIXE spectrum of river water in Meghalaya.

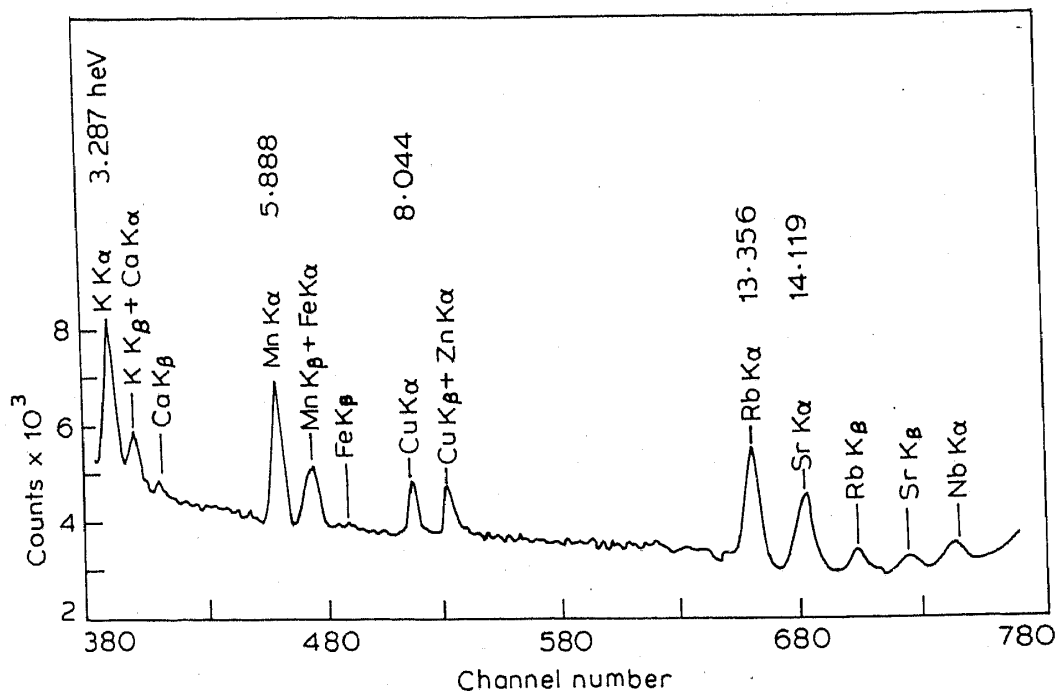


Figure 6. Trace elements in a typical sample of tea.

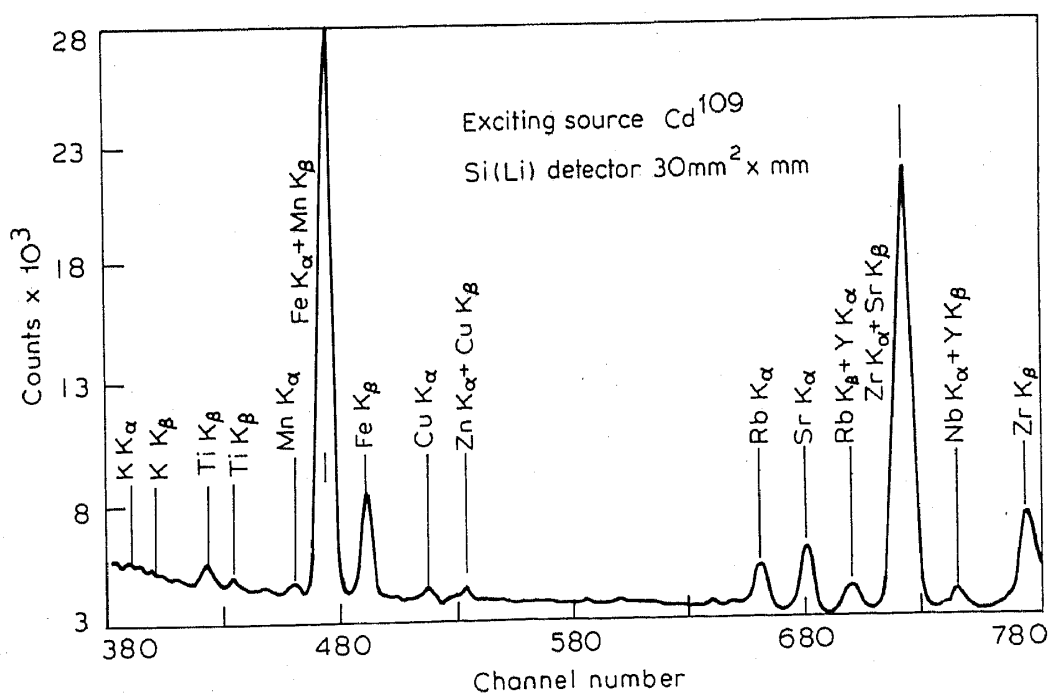
is a shrub with fragrant white flowers and evergreen leaves. The names tea (or cha) are of Chinese origin. The role of micronutrients for the tea plant is quite important. Micronutrients required for the normal health of tea are, <sup>5</sup>B, <sup>12</sup>Mg, <sup>17</sup>Cl, <sup>19</sup>K, <sup>25</sup>Mn, <sup>26</sup>Fe, <sup>29</sup>Cu, <sup>30</sup>Zn and <sup>42</sup>Mo.

Trace elements in tea and in the corresponding soil were studied using the EDXRF

technique for a number of tea and soil samples obtained from the Tea Exporter's Association, Calcutta, Tea Research Association, Jorhat, Assam and the open market, (Madan Lal 1987, Madan Lal *et al* 1987). Typical results are shown in figure 6. A large number of elements in various concentrations are seen and a quantitative evaluation of these elements is shown in table 2. Variations for some of the elements are quite significant. An X-ray spectrum of a soil sample from a tea field is seen in figure 7. The same elements, which are present in tea leaves are seen, but the

**Table 2.** Quantitative analysis in (parts per million) of tea samples from Tea Research Association, Calcutta.

Sample	Mn	Fe	Cu	Zn	Br	Rb	Sr
1	552	427	84	24	15	76	28
2	822	330	93	81	5	8	16
3	95	306	109	114	7	90	18
4	550	210	54	51	—	44	23
5	586	397	63	56	—	79	26
6	692	421	87	86	—	68	15
7	776	329	101	79	—	80	19
8	171	375	70	40	—	72	23
9	84	491	59	63	—	82	20
10	87	378	90	82	—	102	29
11	641	382	99	62	—	95	25
12	556	288	120	80	—	119	31
13	661	204	59	50	—	115	23
14	838	101	51	26	—	88	18
15	535	277	76	63	—	84	23
Range	80–825	100–500	50–120	25–115	0–15	10–120	15–30



**Figure 7.** Trace elements in soil from a tea field.

proportions are different. Ti and Zr, which are present in the soil, are not taken up at all by the tea plant.

Further studies in collaboration with the Tea Research Association are in progress to understand the effect of trace elements on the productivity and quality of tea.

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