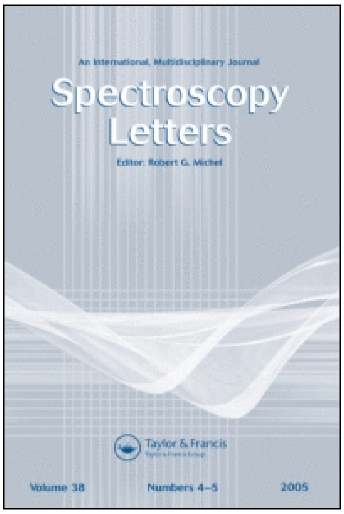

**Spectroscopy Letters**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

# Investigation of Inorganic Contents of Some Diuretic Pharmaceutical Herbs Growing in Turkey by the X - Ray Fluorescence Emission - Transmission (E - T) Technique

N. Efe[a]; H. Yilmaz[b]
[a] Ankara Nuclear Research and Training Center, Saray-Ankara, TURKEY [b] Faculty of Science-Department of Chemistry, Ankara University, Ankara

**To cite this Article** Efe, N. and Yilmaz, H.(1998) 'Investigation of Inorganic Contents of Some Diuretic Pharmaceutical Herbs Growing in Turkey by the X - Ray Fluorescence Emission - Transmission (E - T) Technique', Spectroscopy Letters, 31: 6, 1207 — 1216

**To link to this Article: DOI:** 10.1080/00387019808003296

**URL:** http://dx.doi.org/10.1080/00387019808003296

SPECTROSCOPY LETTERS, 31(6), 1207-1216 (1998)

# INVESTIGATION OF INORGANIC CONTENTS OF SOME DIURETIC PHARMACEUTICAL HERBS GROWING IN TURKEY BY THE X - RAY FLUORESCENCE EMISSION - TRANSMISSION (E - T) TECHNIQUE

Key words : EDXRF , Herbs ,Inorganic contents , E-T method

N. EFE and H. YILMAZ*
Ankara Nuclear Research and Training Center, 06983 Saray - Ankara - TURKEY
*Ankara University, Faculty of Science-Department of Chemistry, Ankara - TURKEY

## Abstract

A radioisotope excited X-ray fluorescence Emission - Transmission (E -T) technique was applied for the determination of inorganic contents of some diuretic pharmaceutical herbs growing in Turkey. Folia Betulae, Stylus Maydis, Flores Verbasci, Equisetum Arvense and Flos Helichrysi herbs which are widely used by public at the cure of kidney diseases were investigated. The study was based on advantages of the XRF E - T method by means of the neglectable enhancement effect and analysis without reference material. An annular source of Cd-109 (3.7 MBq ) was employed for excitation of characteristic K X-rays of the elements in the herbs. Herb samples were prepared in dry and wet forms for the method .The leaching ratios of the elements in these herbs in the period of steeping were calculated. Toxic elements in the considerable amount were not found. It was observed that the other element contents in the dry and wet forms are different.

## Introduction

Energy dispersive X-ray fluorescence (EDXRF) is widely used for the elemental analysis of biological materials. But, this technique has some complexities for quantitative analysis because of interelement and /ore matrix effects[1-3] . Therefore, special attention must be given to overcome the matrix effects in any specimen for which accurate quantitative results are required. Absorption effect is the most important factor resulting from the absorption of both the incident radiation and the characteristic X-rays from the elements in the samples and should be taken into account. Enhancement effect is important but can be neglected in light element matrices such as biological samples[4] . In such cases, only absorption effects contribute significantly. Further, for samples of low atomic numbers, the detection limits for different elements can be improved by determining an appropriate sample thickness. Because, the characteristic X-ray intensity of the trace elements in a sample increases as a function of the thickness only up to certain thickness. Beyond this thickness, the intensity of scattered exciting radiation increases, which in turn decreases the peak - to- background ratio[5] . In biological samples, measurements are usually carried out using thick samples in the form of pellets.

Selection of specimen thickness for optimum detection limits of different elements in biological samples was discussed by Kumar et al[6]. They had used fundamental parameters for the matrix absorption correction. The experimental determination of the absorption correction due to the matrix composition was checked by comparing it with theoretical estimates for a cellulose matrix which is more or less identical with the biological matrix. The suitability of this method was further checked by determining trace element concentrations in different NIST biological standards.

Yawen et al. had described a method for direct determination of trace elements in light element matrices. The intensity of Compton scattering of the incident X-rays from the specimen was used to determine the apparent absorption factor for direct correction for matrix effects[7].

In this study, the X-ray fluorescence E-T method was used for determining the trace elements in five diuretic pharmaceutical herbs namely ***Folia Betulae, Stylus Maydis, Flores Verbasci, Equisetum Arvense and Flos Helichrysi*** growing in Turkey which are effectively used for treatment of kidney diseases by the public. It was shown that standardless XRF E - T method is suitable for light element matrix of biological samples . In this method, the concentrations of the elements in the samples were determined via matrix absorption factors of the elements. Only a thick target consisting of Ca, Ti, Mn, Zn, Se, Zr compounds and cellulose was required for obtaining the efficiency curve of the Si(Li) detector. It is standardless, convenient and precise method for determination of trace elements in low atomic number matrices.

## Theoretical

The fundamental equation of the E-T method is

$$I_i = I_0 G_0 \varepsilon(E_i) K_i C_i m_p f_{abs} \tag{1}$$

where,

$I_i$ is the characteristic x- ray intensity of the element i,

$I_0$ is the intensity of primary radiation ,

$G_0$ is the geometric factor,

$\varepsilon(E_i)$ is the detector efficiency at $E_i$ fluorescence energy of element i,

$K_i$ is a factor which depends on excitation of element i ($K_i$ contains all the fundamental parameters),

$C_i$ is the concentration of the element i in the sample,

$m_p$ is the sample thickness (mass per unit area in g/cm$^2$) and

$f_{abs}$ is the absorption correction factor.

The absorption correction factor is given as follows:

$$f_{abs} = \frac{1 - \exp\left[-X(E)m_p\right]}{X(E)m_p} \tag{2}$$

where,

$X(E)$ is the apparent absorption factor given by

$X(E) = \mu(E_i)\ \mathrm{cosec}\psi_2 + \mu'(E_0)\mathrm{cosec}\psi_1$ .

Here, $\mu(E_i)$ and $\mu'(E_0)$ are the mass absorption coefficients of the specimen for the characteristic radiation of energy $E_i$ and the primary radiation, respectively. $\psi_1$ and $\psi_2$ are the incident and take off angels for the instrument geometry, respectively.

The product of X(E) and $m_p$ is written as

$$X(E)m_p = \ell n\left(\frac{I_i^T}{I_i^{TS} - I_i^S}\right) \quad , \qquad (3)$$

where,

$I_i^S$ , $I_i^{TS}$ and $I_i^T$ are the fluorescent intensities from the sample, from the sample plus target and from the target, respectively.

## Experimental

Five diuretic pharmaceutical herbs such as Folia Betulae, Stylus Maydis, Flores Verbasci, Equisetum Arvense and Flos Helichrysi growing in Turkey were selected. They were commercially obtained in the form of dry tea bags.

In this study, the X-ray fluorescence E -T method was applied firstly for investigating the inorganic contents of this type of herbs. Qualitative and quantitative analysis of these herbs in either dry or wet forms were realised.

Dry herbs were grinded. A large number of pellets of 300 mg with the diameter of 31.7 mm from each herb powder were prepared under a pressure of 15 ton/inch$^2$ . For drug tea analyses, herbs were steeped for ten minutes in boiling water, and then filtered. A specific amount from each teas was added to 1.0 g pure cellulose and dried. Pellets of 300 mg were prepared from these samples of five herb teas with cellulose.

The region of intermediate thickness is $1.0 \geq k \geq 0.1$ ($k=X(E)m_p$) [8] for the E - T analysis., X(E) was determined by taking the $\mu(E_i)$ and $\mu'(E_0)$ values from literature[9]. As a result, $X(E)=15.07$ cm$^2$/g , $m_p = 0.038$ g/cm$^2$ and $k = 0.57$ were calculated. Finally, this k value is suitable for the intermediate thickness .

A Cd-109 (370 MBq) excitation source was selected for providing 22 to 25 keV primary beam energies. Its x-ray lines are located slightly above the absorption edge of the elements in the herbs.

Measurements were performed with an energy dispersive XRF spectrometer consisting of a Si(Li) detector with resolution of 180 eV at 5.9 keV connected to a Canberra - 85 MCA and interfaced to an IBM-PS/1 computer. Comparative XRF spectra of dry and tea samples of Folia Betulae herb is given in Fig. 1. The net peak intensities belonging to five herbs were calculated using an AXIL software program.

## Results and Discussion

The absorption factors belonging to elements in the herbs were calculated by using Eq.3. The concentrations of the elements were determined employing these absorption factors in Eq.1. The results of analysis of dry herbs and herb teas by using the XRF E-T method is given in Table 1.

K : Among five dry herb samples, the maximum concentration of K was 11.4 % . The highest concentration of K was in Stylus Maydis. In the five herb tea samples the maximum concentration of K was 4.96 % in the Folia Betulae.

Ca : Among five different dry herb samples, Ca concentrations were between 3.87% - 0.44 % . The highest value was in Folia Betulae. In the five herb tea samples, Ca concentrations were between 0.81% - 0:09 % . The highest value was in Folia Betulae tea.

Mn : In dry herb samples, Mn was detected in Folia Betulae, Equisetum Arvense and Flos Helichrysi. Concentrations were between 177 ppm - 16 ppm . The maximum. Mn value was in Equisetum Arvense. In the herb tea samples, Mn was only detected in Equisetum Arvense as 75 ppm.

Fe : The concentrations of Fe were between 535 ppm - 218 ppm in the dry samples . The highest value was in Stylus Maydis. In the herb tea samples, Fe concentrations were between 112 ppm - 76 ppm. The maximum concentration of Fe in the drug teas was also in Stylus Maydis.

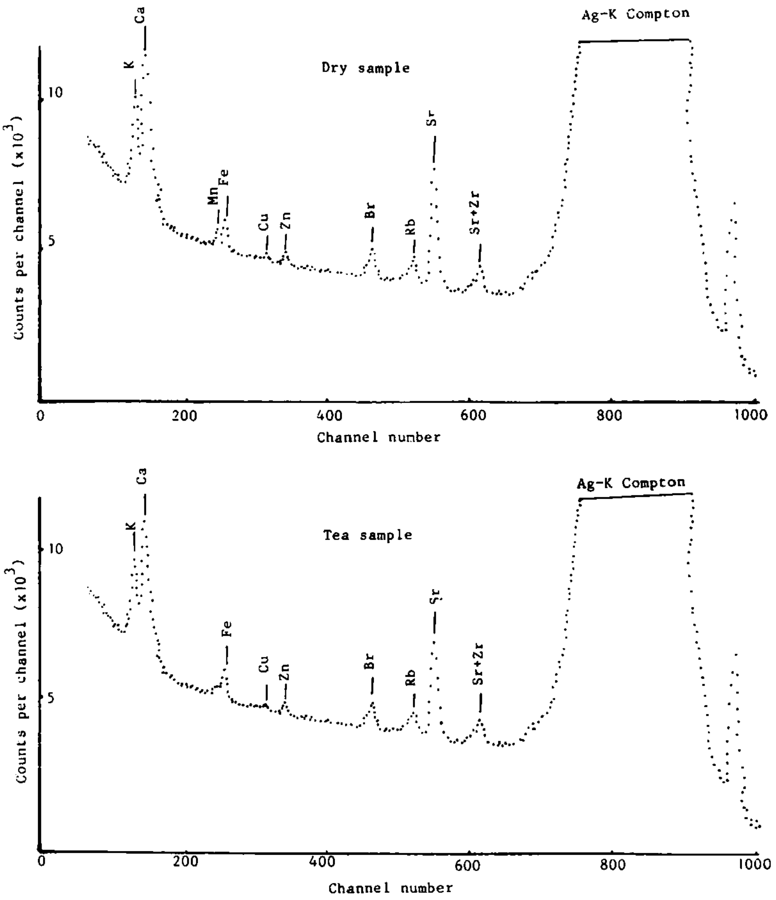

Fig. 1. XRF spectra of dry and tea samples of Folia Betulae

Cu : Among five dry herb samples, Cu concentrations were between 15 ppm - 12 ppm value was in Equisetum Arvense and Stylus Maydis. In the herb tea samples, Cu values were between 11 ppm - 9 ppm . The highest of them was in Flos Helichrysi and Stylus Maydis.

Zn : Zn concentrations were determined between 32 ppm - 9 ppm in the dry herbs. The highest value of Zn was in Stylus Maydis. In the herb teas, Zn was

Table 1. The average concentrations of elements in the herbs from XRF E -T method

| | Folia Betulae | | Stylus Maydis | | Flores Verbasci | | Equisetum Arvense | | Flos Helichrysi | |
|---|---|---|---|---|---|---|---|---|---|---|
| Element | Dry form | Herb tea | Dry form | Herb tea | Dry form | Herb tea | Dry form | Herb tea | Dry form | Herb tea |
| K (%) | 10.8±1.1 | 4.96±0.26 | 11.4±0.5 | 4.77±0.30 | 5.13±0.68 | 2.98±0.13 | 6.28±0.66 | 3.83±0.38 | 5.19±0.26 | 3.72±0.04 |
| Ca(%) | 3.82±0.12 | 0.81±0.03 | 0.44±0.07 | 0.09±0.01 | 1.23±0.14 | 0.28±0.01 | 3.43±0.18 | 0.82±0.07 | 0.81±0.60 | 0.31±0.03 |
| Mn (ppm) | 16.0±3.0 | - | - | - | - | - | 177±13 | 75.0±3.0 | 22.0±3.0 | - |
| Fe (ppm) | 218±13 | 89.0±6.0 | 535±4 | 112±4 | 435±8 | 83.0±4.0 | 428±5 | 76.0±3.0 | 279±9 | 110±9 |
| Cu (ppm) | 12.0±1.0 | 9.00±0.20 | 15.0±1.0 | 11.0±1.0 | 12.0±1.0 | 10.0±1.0 | 15.0±1.0 | 9.00±1.00 | 13.0±1.0 | 11.0±1.0 |
| Zn (ppm) | 17.0±1.0 | 10.0±1.0 | 32.0±3.0 | 9.00±0.30 | 11.0±1.0 | 10.0±1.0 | 20.0±2.0 | - | 9.00±1.00 | - |
| Br (ppm) | 73.0±2.0 | 69.0±3.0 | 52.0±2.0 | 50.0±1.0 | 42.0±2.0 | 42.0±1.0 | 50.0±2.0 | 46.0±2.0 | 45.0±1.0 | 44.0±3.0 |
| Rb (ppm) | 21.0±0.2 | 12.0±1.0 | 25.0±2.0 | 11.0±0.7 | 20.0±2.0 | 10.0±1.0 | 25.0±2.0 | 18.0±2.0 | 16.0±1.0 | 12.0±1.0 |
| Sr (ppm) | 156±2 | 57.0±3.0 | 9.00±1.00 | 3.00±0.30 | 11.0±0.3 | 3.00±0.30 | 45.0±3.0 | 11.0±1.0 | 11.0±1.0 | 2.00±0.20 |
| Zr (ppm) | 4.00±0.60 | 4.00±0.30 | 5.00±0.50 | 3.00±0.30 | 4.00±0.40 | 2.00±0.20 | 4.00±0.40 | 2.00±010 | 6.00±0.70 | 3.00±0.30 |

detected in Folia Betulae, Stylus Maydis and Flores Verbasci between 9 ppm -10 ppm.

Br : Br concentrations were between 43 ppm - 73 ppm in the dry samples. The maximum Br value was in Folia Betulae. In the tea samples , Br concentrations were between 43 ppm -69 ppm. The highest value was in Folia Betulae.

Rb: Rb concentrations were between 16 ppm - 25 ppm in the dry herbs . The maximum Rb value was in Stylus Maydis and Equisetum Arvense. Rb concentrations were between 10 ppm - 18 ppm in the tea samples .The maximum value was in Equisetum Arvense.

Sr : Strontium concentrations were determined between 9 ppm - 150 ppm in the dry herbs . The maximum value was in Folia Betulae. In the herb tea samples, concentrations were between 2 ppm - 57 ppm. The maximum Sr was in the Folia Betulae.

Zr : Among five dry herb samples, the concentrations of Zr were determined between 4 ppm - 6 ppm. In the tea samples ,these values were between 2 ppm. - 4 ppm .

## Conclusion

Trace elements are very important in medicine for the human health . We don't have enough and satisfactory knowledge of the trace element contents of plants using as drug. If we achieve these initial goals, there will be some more areas requiring investigation of trace elements . Trace element contents of plants using as diuretic, cardiotonic, expectoran etc. may be effected by several factors such as soil composition, plant species and maturity and the choice of part.

It was observed that this type of herbs were not investigated for human health in detailed and probable negative effects for human body were not determined adequately in Turkey. Folia Betulae, Stylus Maydis, Flores Verbasci, Equisetum Arvense and Flos Helichrysi herbs are widely used by public at the cure of kidney diseases tra ditionally and randomly.

Table 2. The leaching ratios of the elements in the herbs (%)

| Element | Herb | | | | |
|---|---|---|---|---|---|
| | Folia Betulae | Stylus Maydis | Flores Verbasci | Equisetum Arvense | Flos Helichrysi |
| K | 46 | 42 | 58 | 61 | 72 |
| Ca | 21 | 20 | 23 | 24 | 38 |
| Mn | - | - | - | 42 | - |
| Fe | 40 | 21 | 19 | 18 | 40 |
| Cu | 75 | 73 | 83 | 60 | 85 |
| Zn | 59 | 28 | 91 | - | - |
| Br | 95 | 96 | 100 | 92 | 98 |
| Rb | 57 | 44 | 50 | 72 | 75 |
| Sr | 37 | 33 | 27 | 24 | 18 |
| Zr | 100 | 60 | 50 | 50 | 50 |

Ten elements were determined in flora, folia and herba of five diuretic herbs growing in Turkey by using energy dispersive x-ray fluorescence spectrometer.

In these herbs which are used in the cure of kidney diseases , toxic elements were not found in the harmful concentration ratios. The leaching ratios of elements in these herbs were calculated in the period of steeping for ten minutes (Table 2.). It was observed that the element contents in dry and wet forms are found different.

Such data may be useful in the study of nutrition and public health from the view of trace and toxic elements.

Our further studies will be oriented to the standardisation of this method in order to control of the results determined.

## REFERENCES

1. Rasberry S.D and Heinrich K.F.J., Calibration for Interelement Effects in X-Ray Fluorescence Analysis. Anal. Chem., 1974; 46 : 81

2. Van Grieken R.E , Markowicz A.A. *Handbook of X-Ray Spectrometry* . N .York , Basel , Hong Kong : Marcel Dekker , 1993.
3. Tertian R. Mathematical Matrix Correction Procedures for X-Ray Fluorescence Analysis . X-Ray Spectrometry , 1986 ; 15 : 177.
4. Jenkins R , Gould R.W and Gedcke D . *Quantitative X-Ray Spectrometry.* N.York , Basel : Marcel Dekker , 1981.
5. Giauque R .D , Goulding F.S, Jaklevic J.M and Pehl R.H. Trace Element Determinatin with Semiconductor Detector X-Ray Spectometer. Anal. Chem., 1973 ; 45 : 671.
6. Kumar S , Singh S , Mehta D , Garg M .L , Mangal P .C and Trehan P .N. Matrix Corrections for Quantitative Determination of Trace Elements in Biological Samples Using Energy Dispersive X-Ray Fluorescence Spectrometry. X-Ray Spectrometry ,1989 ; 18 : 207.
7. Yawen L. , Qinmin F and Daolun L . X-Ray Fluorescence Determination of Trace Elements in Complicated Matrices . Adv. X-Ray Analysis ,1986 , 30 : 309.
8. Tertian R and Claisse F . Principles of Quantitative XRF Analysis X-RayR.Tertian, F.Claisse, *Principles of Quantitative XRF Analysis*, London : Heyden , 1982 .
9. Hubbell . J .H , McMaster . W .H , Del Grande. N .K , Maletter. J..M . *International Table for X-Ray Crystallography*, Ibers and Hamilton, Birmingham : Kynoch Press, 1974 .

Date Received: March 12, 1998
Date Accepted: May 7, 1998