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Determination of metals in electronic cigarette refill liquids using Total Reflection X-Ray Fluorescence and PCA analysis

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1. Introduction

Electronic cigarettes (e-cigarettes) are devices which simulate the conventional cigarette, producing an aerosol by heating an e-liquid, which is composed of vegetable glycerin, propylene glycol, flavorings and nicotine. An emerging question is their impact on human health and the purity on the production of these liquids. Some metals were found in e-liquids refills [1,2] as well as emitted by the resistance heating element [3].

To determine metal concentrations in e-liquids, Total Reflection X-Ray Fluorescence spectrometry (TXRF) exhibits diverse advantages, ease sample preparation, low matrix effect, a rapid and simultaneous multi-element analysis, low detection limits (ppb level) and a small sample amount needed to analysis (μL) [2]. Moreover, this approach may be an alternative to certified techniques commonly applied on the literature, e. g. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [2,3].

The purpose of this study is to present a method to e-liquid sample preparation and its metals quantification by TXRF. Furthermore, employ Principal Component Analysis (PCA) [4] as an exploratory statistical method to determine possible correlations about its metal concentrations.

2. Methodology

The measurement system consists of a benchtop TXRF spectrometer (S2 PICOFOX ™, Bruker Nano GmbH, Germany), equipped with a molybdenum (Mo) X-ray tube, operating at 50 kV and 0.6 mA. Sample preparation was proceeded using 1 mL of e-liquid or e-liquids constituents. A Gallium internal standard at 196.00 μg/L was used, 10 μL of this mixture was pipetted three times on a clean and siliconized quartz carrier and left to dry in an oven at 150 ºC, totalizing a thin layer of 30 μL. The analysis was performed in triplicate by 500 s, with a 90º rotation between each measurement.

Distinct brands of e-liquids and flavorings were acquired in local markets, as well as vegetable glycerin, propylene glycol and liquid nicotine. The samples were separated in 3 groups, e-liquids, flavorings, and constituents, shown in Table I.

Table I: Samples of E-liquids, Flavorings and Constituents.

E-Liquids	
Code	**Description**
EX1	Lime Soda
EX2	Strawberry Cheesecake
EX3	Dragon Fruit
EP1	Cream Pie
EP2	Strawberry Pie
EG1	Coconut Cheesecake
EG2	Hazelnut Ice Cream
EG3	Pina Colada
EF1	Strawberry
EF2	Green Apple

Constituents	
Code	**Description**
PG	Propylene Glycol (USP)
VG	Vegetable Glycerin (USP)
NIC	Nicotine (100 mg/ml)

Flavorings	
Code	**Description**
FN1	Hazelnut
FN2	Pecan
FN3	Peanut
FC1	Cheesecake
FC2	Vanilla
FC3	Vanilla Ice Cream
FF1	Orange
FF2	Watermellon
FF3	Pineapple
FB1	Blackberry
FB2	Raspberry
FB3	Strawberry
FT1	Tobacco
FT2	Pipe Tobacco
FT3	Tobacco and Caramel

Total Reflection X-Ray Fluorescence was performed in all samples and the spectrum was acquired by the software Spectra (Bruker Nano GmbH, Germany). The unsupervised method of Principal Component Analysis (PCA) was applied aiming to find correlations between e-liquids metal concentrations. The software R was used for this implementation.

3. Results and Discussion

After analysis of all samples, the average concentrations of metals for each group were taken, shown in Table II.

Table II: Average concentrations of metals by group.

	(Average Concentration ± SD) (µg/L)					
Element	**E-Liquids**	**SD**	**Flavorings**	**SD**	**Constituents**	**SD**
K	3009	17	4243	11	791	10
Ca	799	9	524	3	482	6
Ti	27.2	1.4	14.0	0.6	50.0	1.3
Cr	2.4	0.6	1.3	0.2	3.9	0.3
Mn	7.1	0.6	7.4	0.3	4.4	0.3
Fe	581	13	139	1	613	4
Ni	4.0	0.3	1.9	0.1	7.8	0.3
Cu	18.6	0.6	8.7	0.2	13.0	0.4
Zn	208	24	967	2	93.7	0.9
Br	4.1	0.2	19.0	0.1	4.2	0.1
Rb	9.1	0.3	1.1	0.1	0.0	0.0
Sr	3.2	0.3	5.4	0.2	3.8	0.1

A typical TXRF spectrum of electronic cigarette e-liquid (EG3) acquired is shown in Fig. 1. The elements are identified by their peak energies, K-alpha and K-beta lines for Mn, Fe, Ni, Cu, Zn, and Ga as internal standard.

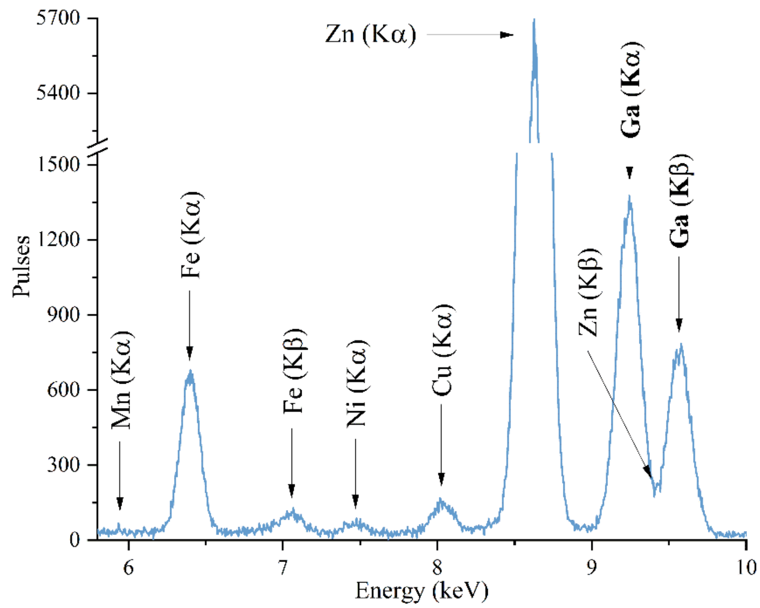

Figure 1: A part of the TXRF spectrum of sample EG3.

Principal Component Analysis (PCA) was applied to determine groupings between e-liquid samples. As shown in Fig. 2, the samples with the same code: X, P, F and G are the same brand. The groups X, P, and F, are commercial e-liquids, the group G are non-commercial e-liquids produced with flavorings and components previously shown.

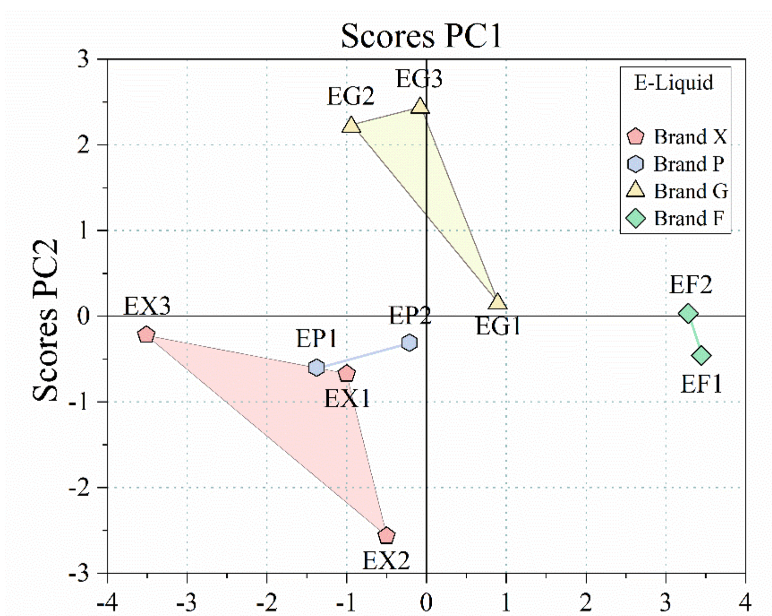

Figure 2: Scores of PC1 and PC2 of E-Liquid samples.

The technique of PCA was capable to discriminate the analyzed e-liquids by its metal concentrations. As shown in Fig. 2, the positive part of the vertical axis (PC2) grouped the non-commercial e-liquids (G samples). The other liquids were grouped in the negative axis. Furthermore, the horizontal axis (PC1) was capable to distinguish the brands F from P and X. These separations between brands can be explained by the loadings where the variables responsible for the positive or negative separation can be observed. The loadings of PC1 and PC2 are shown in Fig. 3.

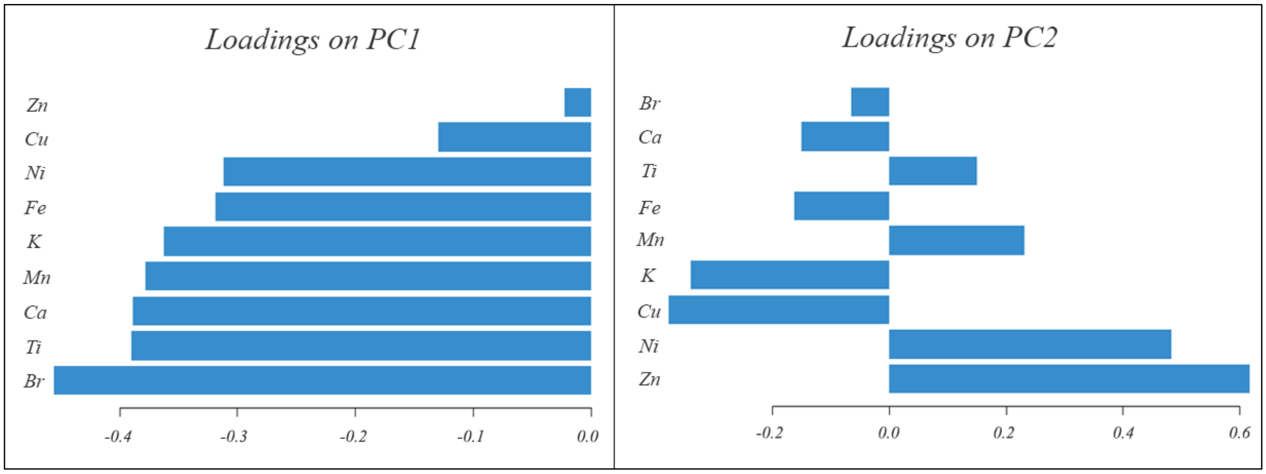

Figure 3: Loadings of PC1 and PC2 of E-Liquid samples.

4. Conclusions

The sample preparation presented in this study showed an ease and fast methodology. The analysis by TXRF reach high sensibility (ppb) and presented a rapid multi-element analysis. Furthermore, in order the high efficiency to analyze metals, TXRF may be a good alternative to the certified techniques commonly applied.

The exploratory method of PCA could separate e-liquids brands by their metal concentrations, showing that the manufacturer's production may be related to different metal contaminations.

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