IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)
e-ISSN: 2319-2402,p- ISSN: 2319-2399.Volume 9, Issue 9 Ver. I (Sep. 2015), PP 55-61
www.iosrjournals.org

Determination of cadmium, iron and tin in home-made Brazilian sugar cane spirit, cachaça by graphite furnace absorption spectrometry using matrix matching calibration

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Summary: *This work reports methods to determine cadmium, iron and tin in home-made Brazilian sugar cane spirit, cachaça using graphite furnace atomic absorption spectrometry (GF AAS) employing matrix matching calibration and zirconium thermally deposited (520 μg) as permanent modifier for iron and tin and none modifier use for cadmium. For Cd, Fe and Sn, the obtained charactetisc characteristic masses (1% absorption) were 0.2; 6.5 and 1.6 pg, with recommended characteristic masses of 0.5, 10 and 5 pg, respectively (Perkin Elmer, Newart, USA). The limits of detection (3α, n=10) were 0.04 pg, 20 and 2.5 pg for Cd, Fe and Sn, respectively. Matrix matching calibration curves (aqueous solutions 40% v/v in ethanol) presented r^2 (linear regression coefficient) greater than 0.999 for all analytes. Two samples of cachaça spiked with 0.75, 1.25 and 1.75 μg L^{-1} showed recoveries from 90.2 to 112.5% for Cd. For iron, the spikes were 30, 60 and 90 μg L^{-1} and recoveries varied between 96.7 to 111.2%, while for tin samples spiked with 15, 25 and 35 μg L^{-1}, recoveries varied between 86.4 to 118.8%.*

Keywords: *Home-made Brazilian sugar cane spirits, cachaça, cadmium, iron, tin, graphite furnace atomic absorption spectrometry, matrix matching calibration.*

I. Introduction

Unlike other alcoholic beverages, Brazilian sugar cane spirits, called *cachaça*, in Portuguese, possesses a very complex composition. The inorganic fraction is constituted mainly by metallic ions, such as aluminum, antimony, cadmium, iron, lead, copper, chromium, tin, lithium, magnesium, manganese, mercury, nickel, potassium, sodium, zinc, among others. These metals probably originated as a result of the fabrication process, or from soil residues, despite some of them being essential to the procedure. The complete chemical composition of *cachaça* remains unknown, because the types and concentrations of the components that compose it are in different matrices (sugar cane) in soil from different areas where the sugar cane is grown, transferring much of these constituents at different concentrations according to what the plant absorbs and metabolizes in relation to the intrinsic characteristics of the soil where it is planted [1, 2].

Cadmium is a non-essential element in humans and potentially poisonous in low concentrations. The first mention of its poisonous effects in humans was reported by Sovet, in 1858 [3]. Only over the last several decades has there been a significant increase in the number of studies performed regarding this metal. In Japan, in 1950, illnesses such as osteomalacia and proteinurie were caused by the ingestion of Cd-polluted foods. Back then, cadmium became one of the most researched metals, and results showed it to have a long biological half-life of 10–30 years, resulting in a cumulative increase in body load, by age, in muscles, kidneys and in the liver [4]. Additionally, as a result of ingestion of Cd polluted foods, the metal could cause renal damage and metabolic calcium disturbances [5]. Thus, a serious health threat can potentially arise even from low-level chronic exposure.

Iron is a relatively abundant element throughout the universe. A telluric element, abundant, composing 30% of the total mass on the planet, almost all rocks and soil contain at least some form of this metal. Among the principal uses of iron in industry includes industry metal works, where it is used mainly as an iron powder, acting as a catalyst in chemical reactions important to steel, the production of magnets, paint, pigments, and abrasives. Therefore, iron is an essential element for the biota [6].

The population in general is exposed to iron mainly through food and beverage consumption [7]. According to the institute of medicine, the daily requirement of iron varies between 8 to 27 mg/day, depending on age and gender and is supplied by a balanced, medium diet. The total medium iron ingestion consumed in

foods is ~15 mg/day. Iron is more easily absorbed in ferrous state [Fe^{2+}], however, most of the alimentary iron is absorbed in ferric form [Fe^{3+}]. Total amount of iron absorbed by the organism is equal to its losses and varies between 3 to 6% of the total amount ingested [8]. Iron deficiency in humans is predominately seen as a lack of dietary protein consumption, resulting in anemia, which if untreated, can advance to more serious forms, such as an alteration of the muscular metabolism and the dysfunction of the immunological system [9]. Iron soluble salts can be irritating to the skin, and when inhaled in dust particle form, and if exposure is prolonged, may cause asthma, diarrhea and even serious fibrotic lung diseases such as silicosis [10]. The toxicity of other iron compounds is due to the associated iron radical. Arsenate and ferric arsenide possess poisonous properties corresponding to arsenical compositions. The pentacarbonil iron, abbreviated as $Fe(CO)_5$, is just one of the components of a larger toxicity that contains carbonyls [10].

Inorganic tin salts are poorly absorbed and rapidly excreted in the feces. As a result, they have low toxicity. Only about 5 percent is absorbed from the gastrointestinal tract, widely distributed in the body, and then excreted by the kidneys. Some tin is deposited in the lungs and bones. Some tin salts can cause renal necrosis after exposure to parenteral doses. Mutagenic studies on metallic tin and its compounds have been negative. Long-term animal carcinogenic studies have shown the presence of malignant tumors in animal models and in human peripheral lymphocytes *in vitro* exposed to tin compared to controls [11, 12]. Human volunteers developed mild signs of toxicity with tin, given in fruit juices, at a concentration of 1400 mg per litre [13]. Amounts in excess of 130 mg per day have been shown to accumulate in the liver and kidneys [14]. Tin deficiency has not been described in man.

One of the main objectives of this study included the study of tin in artisanal (home-made) *cachaças* produced in the state of Minas Gerais – Brazil, because most of these producers use artisanal lead and tin based "soft" weld to solder holes in their distillers, many of which are made of bronze, brass and other metal base materials which includes metal drums used for storage and transportation of diesel fuel.

Soft tin and lead solders are commercially available in just about any hardware store. Soft tin solder is preferred by Brazilian homemade *cachaça* producers as it is inexpensive. Tin concentrations in solder vary between 5% and 70% by weight [15]. This material and other inexpensive methods to produce this alcoholic beverage allow producers to sell their *cachaça* inexpensively, often selling it illegally without any consideration to quality control standards.

The selection of the permanent modifiers zirconium and ruthenium in this study was based on good results obtained with these modifiers in previous studies [16-25].

Therefore, in the present study, we proposed the use of graphite furnace atomic absorption spectrometry using matrix matching calibration and zirconium as a permanent modifier to determine iron, tin and none modifier use to determine cadmium as a procedure to analyze these metals in artisanal Brazilian *cachaça* samples from 52 producers.

II. Experimental

Instrumentation

All measurements were carried out with a Perkin Elmer (Newart, NJ, USA) analyst 400 atomic absorption spectrometer, equipped with a graphite furnace HGA 900, an autosampler as 800 (Perkin Elmer) and deuterium arc lamp background correction, operated under recommended conditions, according toby the manufacturer. Integrated absorbance (peak area) was used exclusively for signal evaluation. The lamps were purchased from Perkin Elmer. An electrodeless lamp for Cd (part no. 305-0615) was operated at 210 ma, with a 2.7-1.35 slit and 228.80 nm wavelength. The electrodeless Sn lamp (part no. 305-0675) was operated at 280 ma, with a 2.7-1.05 slit and wavelength of 286.33 nm. A hollow Fe cathode lamp (part no. 305-0212) was operated at 20 ma, with a 1.8-1.35 nm slit and 248.33 nm wavelength. The volume added into the graphite tube was 20 μL for the sample and the matrix matching calibration solutions. The tubes were treated with zirconium and ruthenium, as described previously [16, 26], i.e. employing a 100 μL of Zr (1000 mg l^{-1}) and submitting the tube to the temperature program. This procedure was repeated five times in order to obtain a deposit of 500 μg of the metals. For platform treatment, the same program was used. In this case, we used a 40 μL solution Zr or Ru (1000 mg l^{-1}) and the procedure was repeated 13 times to obtain the same deposit of 520 μg of the metals on the platform. Argon, 99,996 % (White Martins, Belo Horizonte, MG, Brazil), was used as a sheath gas. Graphite tubes, with integrated platforms (Perkin Elmer, part number B3001264 and B3001263), were used for all studies. The graphite furnace temperature programs for determination of the analytes were optimized and are shown in Table 1.

Reagents and solutions

All chemicals used were of analytical-reagent grade, unless specified. Water was de-ionized in a Milli-Q system (Millipore, Bedford, MA, USA). The ethanol used to prepare the matrix matching calibration curves was from Aldrich, (Milwauke, WI, USA) No. 20.699-7. The cadmium, iron and tin analytical solutions were

prepared from stock solutions of 1000 mg L^{-1}, prepared using 5%v/v nitric acid from ampoules (Titrisol, Merck, Germany) and stored according to the manufacturer's instructions. Ruthenium, from Fluka (Buchs, Switzerland, No 84033) and zirconium (Aldrich, No.27497-6) solutions were prepared at 1 mol L^{-1} in hydrochloric acid and were used to obtain the permanent modifiers. All glassware were washed thoroughly with detergent solutions, rinsed with water, placed in a nitric acid 20% v/v bath for more than one hour, and finally, prior to use, rinsed several times with deionised water. The autosampler cups were submitted to the same treatment.

Procedure

The matrix matching calibration curves were prepared for both elements in aqueous solutions containing 40 % v/v in ethanol, since the alcoholic average grade in *cachaça* is about 40% v/v in ethanol. The accuracy of the proposed methodology was verified by recovery of *cachaça* samples spiked with 0.75, 1.25 and 1.75 μg l^{-1} of cadmium; 30, 60 and 90 μg l^{-1} of iron and 15, 25 and 35 μg l^{-1} of tin. Recovery studies were performed in two samples against matrix matching calibration curves. The limit of detection (LOD, μg l^{-1}) was calculated using the equation LOD = 3 x s_{bl}/b, where s_{bl} is the standard deviation of ten measurements of the blank (aqueous solution 40% v/v in ethanol) and *b* is the slope of the matrix matching calibration.

III. Results and Discussion

In order to investigate the behavior of pyrolysis and atomization of cadmium, iron and tin in the *cachaça* samples, the respective pyrolysis and atomization temperature curves were obtained for each metal with and without modifier use. Figure 1 presents the curves produced for pyrolysis and atomization of cadmium in *cachaça* samples.

An extremely important fact observed when analyzing Figure 1 is that the sensitivity for cadmium remains virtually unchanged without the use of chemical modifier, as seen from extremely low temperatures, such as 300 °C to about 1200 to 1300 °C.

In examining sensitivity, the characteristic mass obtained was 0.2 pg, which was less than half the characteristic mass recommended by the equipment manufacturer, or 0.5 pg (Perkin Elmer). During a thorough review of the scientific literature on this subject, we found no such published articles, in which, without the use of modifier, cadmium is stable at temperatures above 300-400 °C. Since the study was done using a sample of *cachaça*, it can be assumed that either the *cachaça* or alcohol present in the beverage itself may have acted as a thermal stabilizer for this analyte at such high temperatures, which will be the subject of future investigations.

In a study performed to determine cadmium in wines [27] using an optimized value of 15 mg of Pd as chemical modifier, with an optimum temperature of 1300 ºC for atomization, the authors obtained a pyrolysis maximum temperature of 600 °C, with a 10 second pyrolysis time. Additionally, the authors obtained a characteristic mass for metal of 0.7 pg with a detection limit (LOD) of 0.03 pg for a sample volume of 20 μL.

Finally, the authors obtained a slope of 0084 ± 0002 (n = 3) for aqueous curves, while the mean slope for the curves for a standard addition of six wine samples was 0.121 ± 0.006 (n = 6) and this result was used to calculate the concentrations in the analysis of 30 Brazilian wine samples.

In a study conducted by Silva et al. [22], using biological samples solubilized with tetramethylammonium hydroxide by ET AAS (elecrothermal atomic absorption spectrometry), and using ruthenium (500 μg) as a permanent modifier, the pyrolysis and atomization temperatures were chosen from the pyrolysis and atomization temperature curves at 750 and 1300 ºC, and were optimized as the best pyrolysis and atomization temperatures for cadmium, respectively. Bulska et al. [28], investigating palladium, rhodium and iridium electrodeposited on the graphite surface, and using cadmium as a testing element, maximum pyrolysis temperatures were 800°C, with Ir as modifier, 900°C with Pd, 1000°C with Pd+Rh, and 1100°C with Rh alone.

In a study using graphite multielement furnace for As, Cd, Cu and Pb in wines introduced directly into the graphite furnace, the authors obtained a pyrolysis temperature of 600 ºC (with an atomization temperature of 2200 ºC) for the studied group elements using 5 μg of Pd (as nitrate) plus 3 μg $Mg(NO_3)_2$ as chemical modifier. The LOD obtained for cadmium in this study was 0.03 μg L^{-1} [29, 30], investigating the direct determination of Cu, Pb and Cd in aniseed spirits by ET AAS, resulting in the best sensitivity obtained using palladium nitrate (43 mg L^{-1}) at a pyrolysis temperature of 500 ºC. This result was better than using magnesium nitrate (25 mg L^{-1}), Pd-Mg nitrates (43-25 mg L^{-1}) and non matrix modifier.

In a study by da Silva [17], investigating the behavior of atomization of Au, Ag, Bi, Cd, Pb, and Sn in aqueous solutions (nitric acid 0.2% v / v), and in ethanol, studying the use of non-modified, the author used a universal mixture for Pd plus Mg and permanent Zr. The authors reported that the gain in sensitivity was about three times greater (relative to the characteristic mass recommended by the manufacturer) for Bi and Cd when using Zr as permanent modifier. Without the use of modifier, the ethanol medium is suitable for Au and Cd, which had a maximum sensitivity between the modifiers tested without using non modifier with pyrolysis and atomization temperatures of 950 and 1500 °C, respectively for gold, and 400 to 1100 ºC for cadmium.

In the presented results, the subsequent investigations and metal analyzes were performed without the use of modifier.

For iron (Figure 2), the most sensitive condition was achieved using permanent zirconium (520 mg), with pyrolysis and atomization temperatures reaching 800 and 2500 °C, respectively. In this case, the characteristic mass obtained was 6.5 pg, less than that recommended by the manufacturer of 10 pg (Perkin Elmer).

Naozuka and Oliveira [31] investigated the use of dilutions with nitric acid 0.1% v /v only for the determination of Al, Cu and Fe in coconut water by ET AAS. In iron, 100 mL of samples were diluted with 1400 µL solution of 0.1% v/v of nitric acid and 10 µL aliquots of this solution were introduced into the graphite furnace without the use of chemical modifiers. The maximum pyrolysis temperature without loss of signal obtained for iron was 1200 °C. According to the authors, the high dilution factor, combined with the thermal stability of the analyte, explained the use of non-modifiers. Ollala et al. [32] compared different methods for determination of iron in alcoholic beverages (table wines, grape juice, white wines, sweet wines, brandies and anisettes) by ET AAS. According to their results, the best results applied to all types of samples were obtained for wet mineralization with heated acid (HNO_3-H_2SO_4). The LOD obtained for iron was 19.2 µg l^{-1}.

Analytical figures of merit

Two *cachaça* samples spiked with different amounts of cadmium (0.75, 1.25 and 1.75 µg l^{-1}) showed recoveries between 99.2 to 112.5% (Table 2), with an RSD % (n=3) less than 2%. The LOD (k=3, n=10) was 0.04 pg for the 52 samples from 52 different home-made *cachaça* producers. The cadmium results varied from non detectable to 1.025 µg l^{-1} (Table 3). Brazilian legislation does not regulate allowable Cd value limits in alcoholic beverages.

Two samples spiked with iron (30, 60 and 90 µg l^{-1}) presented recoveries from 96.7 to 111.2% (Table 4), with an RSD % (n=3) less than 2.3 % and the LOD was 20 pg. For the 52 samples, the iron values varied from non detectable to 3.58 µg l^{-1} (Table 5). Like Cd, Brazilian legislation does not regulate allowable Fe value limits in alcoholic beverages.

Two samples spiked with tin (15, 25 and 35 µg l^{-1}) presented recoveries from 95.2 to 118.8 % (Table 6), with an RSD % (n=3) less than 2.7 % and the LOD was of 2.5 pg. For the 52 analyzed home-made *cachaça* samples, the values obtained varied between non detectable to 317.30 µg l^{-1} (Table 7). In accordance with Brazilian legislation, the maximum permitted tin concentration in alcoholic beverages is 150 µg l^{-1} [33]. It was observed that in some of the distillers (lead-tin) used for *cachaça* production, the welding was made with soft solder, which may be a probable source of Sn contamination of the analyzed home-made *cachaça* samples.

IV. Conclusions

We conclude that cadmium, iron and tin in home-made *cachaça* samples can be determined with good accuracy and precision by GF AAS without using a modifier for Cd and using a permanent Zr modifier (520 µg) for iron and tin, and also using matrix-matched calibration. It is also possible that *cachaça* itself acts as a modifier. The recovery for samples spiked with Cd, Fe and Sn showed values close to 100%, thus assuring good accuracy. It should be pointed out that 12 samples of *cachaça* (in the 52 samples analyzed) showed tin concentrations greater than 150 µg l^{-1}, the maximum allowable tin concentration for alcoholic distilled beverages, which is in agreement with Brazilian legislation (Brazil, 1998). Thus, the contamination found in some of the *cachaça* samples is of grave concern, particularly when used for human consumption.

Acknowledgements

The authors wish to thank the Conselho Nacional de Pesquisa e Desenvolvimento Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) e a Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES). J. B. B. Silva was awarded a fellowships from CNPq.

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List of tables

Table 1. Temperature program for the determination of the metals in cachaça samples.

Step	Temperature, °C	Ramp, S	Hold, S	Ar flow rate (ml min^{-1})
1	90	5	10	250
2	140	5	10	250
3	1000[a], 800[b], 1800[c]	10	10	250
4*	1500[a],2500[b], 2300[c]	0	5	0
5	2600	1	5	250

*Reading in this step; a = Cadmium; b = Iron and c = Tin.

Table 2. Recovery values for two cachaça samples spiked with cadmium.

Sample A				Sample B			
Expected (µg L^{-1})	Determined (µg L^{-1})	Recovery, %	RSD (n=3)	Expected (µg L^{-1})	Determined (µg L^{-1})	Recovery, %	RSD (n=3)
0.75	0.793	105.7	1.38	0.75	0.844	112.5	0.57
1.25	1.404	112.3	1.52	1.25	1.240	99.2	1.28
1.75	1.786	102.1	1.99	1.75	1.853	105.9	0.15

Table 3.Concentration of cadmium (μg L^{-1}) in Brazilian cachaças samples.

Sample	Determ.	Sample	Determ.	Sample	Determ.	Sample	Determ.
1	Nd	15	0.390	29	Nd	43	Nd
2	Nd	16	0.611	30	Nd	44	Nd
3	0.117	17	Nd	31	0.406	45	0.111
4	Nd	18	0.265	32	Nd	46	Nd
5	Nd	19	Nd	33	Nd	47	0.480
6	Nd	20	Nd	34	Nd	48	Nd
7	0.220	21	Nd	35	Nd	49	Nd
8	Nd	22	1.025	36	0.320	50	0.740
9	0.350	23	Nd	37	0360	51	Nd
10	Nd	24	Nd	38	Nd	52	0.262
11	Nd	25	Nd	39	Nd		
12	Nd	26	0.258	40	0.351		
13	0.480	27	Nd	41	Nd		
14	0.158	28	Nd	42	0.257		

Table 4. Recovery values for two cachaça samples spiked with iron.

Sample A			Sample B		
Expected (μg L^{-1})	Determined (μg L^{-1})	Recovery, %	Expected (μg L^{-1})	Determined (μg L^{-1})	Recovery, %
30	33.36	111.2	30	33.27	110.9
60	61.10	101.8	60	61.80	103.0
90	88.22	98	90	86.99	96.7

Table 5. Concentration of iron (μg L^{-1}) in Brazilian cachaças samples.

Sample	Determ.	Sample	Determ.	Sample	Determ.	Sample	Determ.
1	1.018	15	1.560	29	0.850	43	2.290
2	0.325	16	1.250	30	1.450	44	0.641
3	1.920	17	1.580	31	0.230	45	2.250
4	1.590	18	2.630	32	0.680	46	2.970
5	2.780	19	0.850.	33	0.928	47	3.570
6	0.950	21	Nd	34	0.470	48	0.780
7	0.529	22	Nd	35	0.540	49	0.650
8	0.580	22	0	36	0.250	50	0.780
9	0.870	23	0.250	37	1.680	51	0.730
10	0.950	24	Nd	38	2.220	52	1.226
11	2.020	25	0.120	39	Nd		
12	0.589	26	0.850	40	0.780		
13	0.847	27	0.240	41	2.220		
14	0.822	287	0.360	42	3.580		

Table 6. - Recovery values for two cachaça samples spiked with tin.

Sample A			Sample B		
Expected (μg L^{-1})	Determined (μg L^{-1})	Recovery, %	Expected (μg L^{-1})	Determined (μg L^{-1})	Recovery, %
15	17.82	118.80	15	12.96	86.40
25	23.80	95.20	25	24.11	96.44
35	37.00	105.71	35	33.56	95.84

Table 7. Concentration of tin (μg L^{-1}) in Brazilian cachaças samples.

Sample	Determ.	Sample	Determ.	Sample	Determ.	Sample	Determ.
1	0.870	15	208.100	29	39.840	43	0.450
2	43.020	16	86.260	30	3.681	44	161.100
3	10.340	17	0.695	31	9.964	45	5.304
4	10.490	18	4.779	32	59.950	46	1.866
5	87.490	19	29.750	33	Nd	47	100.700
6	28.020	20	28.400	34	147.000	48	22.530
7	4.879	21	0.696	35	1.117	49	2.510
8	1.403	22	17.210	36	Nd	50	Nd
9	28.500	23	61.780	37	9.057	51	317.30
10	45.400	24	14.280	38	Nd	52	9.608
11	11.600	25	1.562	39	8.499		
12	25.770	26	54.230	40	0.273		
13	38.120	27	31.670	41	16.340		
14	6.871	28	37.250	42	140.600		

List of figures

Fig.1 Pyrolysis and atomization temperature curves for 45 pg of Cd in cachaça samples using permanent ruthenium, permanent zirconium and no modifier.

Fig.2 Pyrolysis and atomisation temperature curves for 0.7 ng of Fe in cachaça samples using ruthenium permanent, zirconium permanent and no modifier.

Fig.3 Pyrolysis and atomisation temperature curves for 0.4 ng of Sn in cachaça samples using ruthenium permanent, zirconium permanent and no modifier.

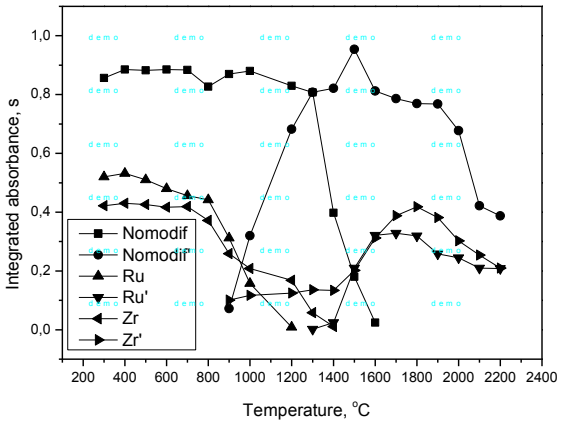

Figure 1

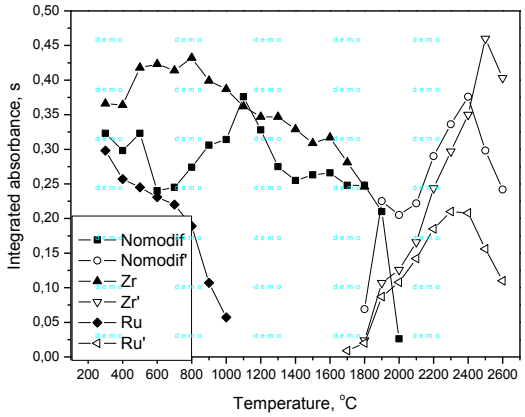

Figure 2

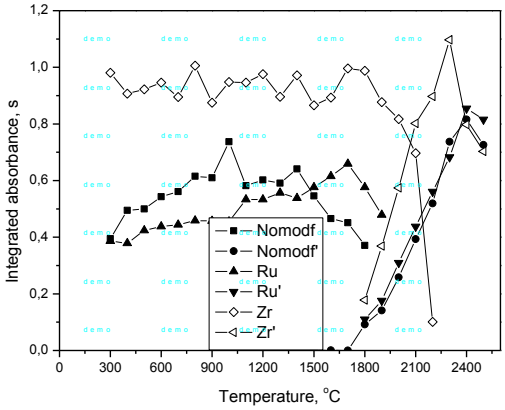

Figure 3