

Simultaneous Determination of Sodium, Potassium, Calcium, Nickel, Chromium, Iron and Zinc in Cathodic Electrodeposition Primers by Using ICP-OES

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Abstract

Na, K, Ca, Ni, Cr, Fe, Zn were determined simultaneously in cathodic electrodeposition (CED) primer with Inductive Coupled Plasma-Optic Emission Spectrometer (ICP-OES) system. 588.995 nm for Na, 766.491 nm for K, 396.847 nm for Ca, 232.003 nm for Ni, 267.747 nm for Cr, 259.941 nm for Fe, 213.856 nm for Zn were monitored in radial view mode at SPECTRO ARCOS instrument with true multiview plasma observation technology. Also, 361.384 nm for Sc was used as internal standard. In sample preparation step, CED primer samples were diluted with a dilution solvent, vortexed and introduced to the instrument for analysis. According to Eurachem The Fitness for Purpose of Analytical Methods second edition (2014), validation was performed to characterize the method for selectivity, limit of quantitation (LOQ), linearity, accuracy, precision, recovery, matrix effect and dilution integrity. For this method, LOQ concentrations for each analytes were found respectively: 0.60 mg/kg (Na, K, Ca, Ni, Cr), 1.00 mg/kg (Fe, Zn). Also, linear calibration curve ranges varied between respectively: 0.60-6.00 mg/kg for Na, K, Ca, Ni, Cr, 1.00-20.0 mg/kg for Fe, Zn. In addition, recovery results were obtained from 80% to 120 % for LOQ concentrations of each analytes.

Keywords: CED coatings, ICP-OES, Corrosion, Waterborne primers, Validation.

Kataforez Kaplamalarda Kullanılan Sulu Astarlardaki Sodyum, Potasyum, Kalsiyum, Demir, Krom, Nikel ve Çinkonun ICP-OES ile Eş Zamanlı Tayini

Öz

Eksiyüçsal elektrikli bırakım astarlarında bulunan Sodyum, Potasyum, Kalsiyum, Nikel, Krom, Demir ve Çinko'nun eş zamanlı tayini İndüktif Eşleşmiş Plazma-Optik Emisyon Spektrometresi kullanılarak gerçekleştirilmiştir. Gerçek çoklu görünüm plazma teknolojisine sahip SPECTRO ARCOS model cihazı ile Sodyum, Potasyum, Kalsiyum, Nikel, Krom, Demir, Çinko için sırasıyla 588.995, 766.491, 396.847, 232.003, 267.747, 259.941, 213.856 nm ve iç standart olarak kullanılan Skandiyum için 361.384 nm dalgaboyları radyal tip plazma bakışı kullanılarak takip edilmiştir. Örnek hazırlama aşamasında, eksiyüçsal elektrikli bırakım astarları dilüsyon solventi ile seyreltilip vortekslenildikten sonra analizi gerçekleştirilmiştir. Yöntemde seçicilik, belirtme alt sınırı (LOQ), doğrusalılık, doğruluk, kesinlik, geri kazanım, matriks etkisi ve dilüsyon doğruluğu incelenip Eurachem The Fitness for Purpose of Analytical Methods ikinci baskısına (2014) göre validasyon gerçekleştirilmiştir. Bu yöntemdeki belirtme alt sınır derişimleri sırasıyla Sodyum, Potasyum, Kalsiyum, Nikel, Krom için 0.60 mg/kg, Demir ve Çinko için ise 1.00 mg/kg'dır. Doğrusal kalibrasyon eğrisi aralığı Sodyum, Potasyum, Kalsiyum, Nikel, Krom için 0.60-6.00 mg/kg, Demir ve Çinko için ise 1.00-20.0 mg/kg'dır. Bununla birlikte, her bir analitin belirtme alt sınırı derişimindeki geri kazanım değerleri %80 ile %120 aralığında yer almaktadır.

Anahtar Kelimeler: CED kaplamalar, ICP-OES, korozyon, sulu astarlar, validasyon.

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CED is superior to AED because of following reasons: excellent corrosion protection, better chemical resistance, less iron dissolution, great throw power and higher detergent resistance. CED has been used in a variety of industries such as the automotive industry, building materials, light industry, household products, etc. due to its excellent corrosion resistance, high penetration rate, dispersion, automation, and minimal pollution. It has a wide range of applications e.g anticorrosion and decorative coatings in industrial areas [1-4]. Blocked polyisocyanates and modified epoxy or acrylic resins are the most common resin components used in CED coatings. Crosslinking mechanism is carried out by linking urethane and/or urea [5]. There has been a noticeable increase using of CED which provide excellent corrosion resistance and low environmental pollution in the coating industry in recent years. CED has managed to maintain its popularity as an anti-corrosion method, and today more than 80% of motor vehicle manufacturers prefer this technique with using of waterborne primer known as cathodophoresis paint. In CED coatings, waterborne primers have been used as film formers. Mostly, typical composition of these waterborne primers is 80-85% deionized water, 10-20% binder (epoxies or acrylics), 1-5% pigments, 1-5% fillers, 1-5% additives and 0.5-1% solvents. CED coating process of passenger and commercial vehicles is carried out in large volumes of baths. Also, vehicle parts need to be coated are dipped in waterborne primer baths [6-10]. This process leads to changes in the content of waterborne primers over time. Increasing concentration of Na, K, Ca, Ni, Cr, Fe, Zn elements in the bath may lead to coating defects. As a result of this, coating companies and their customers suffer from huge losses in terms of time and money. Therefore, quantitative tracking and determination of the mentioned elements in waterborne primers in baths has become more essential. It is a very important task to establish an analytical method for quantification of these metals in baths. There are various sample preparation techniques such as microwave-assisted digestion, wet digestion and dry ashing etc. to determine metals by using atomic spectroscopy in literature. Chaves, S. E et al., used microwave-assisted digestion to determine metals and phosphorus in vegetable seeds by ICP-OES [11]. Wet digestion which is another common sample preparation technique has been preferred to determine metals in paints by Silva, F. L. F et al [12]. Dry ashing is one of the alternative sample preparation technique and is accomplished by heating the sample in an open dish or crucible in air [13,14]. As a result of the evaluation and comparison of the mentioned sample preparation techniques [15,16] which were found to be cumbersome due to long run time, impractical and high cost. Therefore, a rapid, cheap, robust and accurate sample preparation method was developed for this study. To the best of our knowledge, there are no studies dealing with this subject in literature. In this study, a simple, precise and accurate analytical method was developed by using ICP-OES technique in radial plasma view mode for a CED primer and the developed method was validated according to Eurachem Guideline [17].

2. Material and Methods

2.1. Chemicals and Reagents

100 mg/L ICP-MS mixture standard solution (Product Code:ICP250.M280016), 1000 mg/L Zinc, 1000 mg/L Iron, 20000 mg/L Cesium ionization buffer and 1000 mg/L Scandium internal standard solution were obtained from Labsert (Turkey). Redoks-238 standart solution was supplied from Inorganic Ventures (USA). Suprapur Nitric Acid (HNO₃) 69% (Merck, Germany), Suprapur Hydrogen Peroxide (H₂O₂) 30% (Merck, Germany) and Suprapur Hydrochloric acid (HCl) 36% (Merck, Germany) were used for microwave digestion experiments. Sample preparation was conducted using Regaent Plus >99.5 1-Methoxy 2-propanol (Merck, Germany), Acetic Acid 100% (Glacial) (Merck, Germany) and 18.2 MΩ·cm deionized water (Thermo Scientific Barnstead Smart2Pure Water Purification System).

2.2. Instrumentation and Experimental Conditions

All spectrometric experiments were performed by using SPECTRO ARCOS (Germany) ICP-OES analyzer. SPECTRO ICP Analyzer Pro software program was used for peak calculations. ICP-OES method parameters are given in Table 1.

Table 1. ICP-OES method parameters

Parameter	Value
Plasma Power (W)	1450
Coolant Gas Flow (L/min)	12.0
Auxiliary Gas Flow (L/min)	0.80
Nebulizer Gas Flow (L/min)	0.80
Light Tube Flow (L/min)	0.90
Sample Flow (mL/min)	2.00
Overall Measurement Time (s)	129
Replicate Count	3
Nebulizer	Cross flow
Spray Chamber	Scott Type Glass
Torch	Quartz 1.8 mm
Plasma View Mode	Radial

2.3. Calibration Standards

Calibration standards were prepared with dilution solvent for each analyte (Na, K, Ca, Ni, Cr ; 0.60, 1.20, 2.40, 4.00, 6.00 mg/kg, Fe, Zn; 1.00, 2.00, 4.00, 10.0, 20.0 mg/kg). Dilution solvent: 5% Acetic Acid and 5% 1-Methoxy 2-propanol in 18 MΩ·cm deionized water.

2.4. Sample Preparation

1.500±0.005 g CED primer was weighed into 50 mL polypropylene tube. After, 600 µL internal standard solution (Scandium 100 mg/L) and 2.40 mL ionization buffer agent (Cesium 20000 mg/L) were added. In order to carry out a final weight of 30 grams, it was diluted with dilution solvent which contains 5% Acetic Acid, 5% 1-Methoxy 2-propanol in 18 MΩ•cm deionized water and vortexed for 15 minutes. Finally, CED primer sample was submitted to ICP-OES instrument for analysis.

3. Results and Discussion

3.1. Method Development

Optimization studies of sample preparation process was carried out by using microwave-assisted digestion and extraction techniques. Recovery was performed by adding known quantities of all analytes to CED primer consisting of 80% deionized water, 15% binder (epoxy), 1% pigments, 2% fillers, 1% additives and 1% solvents for both techniques. For microwave-assisted digestion, 0.150 g CED primer samples which contain known concentrations for each analytes were weighed accurately into the microwave digestion vessels and added 6 mL 69% HNO₃ (Merck Suprapur), 1 mL 36% HCl (Merck Suprapur), 1 mL 30% H₂O₂ (Merck Suprapur) respectively.

The vessels were capped and placed in the microwave digestion system. During the digestion process, four steps were followed: 25 to 110 °C in 5 min; 110 °C for 5 min; 110–220 °C in 20 min; heated at 220 °C for 15 min. After digestion, each samples were added 300 µL internal standart (100 mg/L Scandium), 500 µL ionization buffer agent (20000 mg/L Cesium) respectively to suppress ionization interferences of easily ionizable elements such as Na, K, Ca and diluted to 15.0 g with 18 MΩ•cm deionized water. Finally, the samples were submitted to ICP-OES instrument for analysis. Based on the results of this experiment (Table 2.), the recoveries were not found to be acceptable (±20%).

Table 2. Recovery results of microwaved asisted digestion

Analytes	Added (mg/kg)	Recovery (mean, n=3) (%)
Na	0.60	78.2
K	0.60	130
Ca	0.60	140
Ni	0.60	110
Cr	0.60	109
Fe	1.00	112
Zn	1.00	110

Recovery= (Found Conc.-Initial Conc.)/(Added)*100

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Besides unacceptable recoveries of Na, K and Ca for this experiment, microwave-asisted digestion technique has various weaknesses such as high energy consumption and long run time. Therefore, liquid-liquid extraction technique was preferred instead of microwave-asisted digestion. In liquid-liquid extraction, 1.50 g CED primer samples which contain known concentrations for each analytes were weighed into 50 mL polypropylene tube. After, 600 μ L internal standard solution (Scandium 100 mg/L) and 2.40 mL ionization buffer agent (Cesium 20000 mg/L) were added. In order to get a final weight of 30 grams, it was diluted with 18 M Ω •cm deionized water. As a result of this experiment, it was found that recovery values of analytes (Table 3.) were lower than expected (80-120%).

Table 3. Recovery results of liquid-liquid extraction with deionized water

Analytes	Added (mg/kg)	Recovery (mean, n=3) (%)
Na	0.60	70.8
K	0.60	67.7
Ca	0.60	78.3
Ni	0.60	75.6
Cr	0.60	75.3
Fe	1.00	70.0
Zn	1.00	80.0

Recovery= (Found Conc.-Initial Conc.)/(Added)*100

pH value of CED baths (generally should be 5-7) is adjusted by using Acetic acid. Also, CED primers typically contain low amount of some solvents such as 1-Methoxy 2-propanol. Considering these factors, 5% Acetic acid and 5% 1-Methoxy 2-propanol were added to 18 M Ω •cm deionized water in order to match polarity with CED primer.

Liquid-liquid extraction process was performed again with %5 Acetic acid and 5% 1-Methoxy 2-propanol in 18 M Ω •cm deionized water. As expected, recovery results were found to be acceptable (Table 9). As a final step, the effect of Cesium concentration to be immune to interferences caused by easily ionizable elements [18] such as Na, K and Ca on recovery was evaluated. It was observed that Cesium did not have a significant effect on recovery (Table 4). It is possible for CED primers to contain excessive amounts of easily ionizable elements such as Na, K, and Ca in unexpected situations. Therefore, 1600 mg/L Cs which has best response in instrument was used to eliminate ionization interferences of these elements.

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Table 4. The effect of Cesium concentration on recovery

Analytes	Concentration	Recovery (mean, n=3) (%)		
	Added (mg/kg)	Without Cs	400 mg/L Cs	1600 mg/L Cs
Na	0.60	96.0	92.0	91.2
K	0.60	86.2	85.1	84.3
Ca	0.60	98.8	91.0	97.1
Ni	0.60	101	103	102
Cr	0.60	97.8	99.2	96.8
Fe	1.00	108	104	106
Zn	1.00	112	108	110

Recovery= (Found Conc.-Initial Conc.)/(Added)*100

In consequence, an analytical method was developed in this study by using ICP-OES system to determine Na, K, Ca, Ni, Cr, Fe and Zn simultaneously. The method was validated according to Eurachem Guideline [17].

3.2. Validation

Validation was carried out with blank CED primer sample consisting of 80% deionized water, 15% binder (epoxy), 4% additives and 1% solvents (Na, K, Ca, Ni, Cr, Fe, Zn-free).

3.2.1. LOQ

The lowest concentration of quality control sample (0.60 mg/kg for Na, K, Ca, Ni, Cr, 1.00 mg/kg for Fe and Zn) was injected 10 times in a row to determine LOQ. Standard deviation (σ) x 10 was used to estimate LOQ.

3.2.2. Selectivity

Peak heights were compared with spiked sample at LOQ concentration and six different blank CED primer samples. Figure 3. shows that there is no interference between Na, K, Ca, Ni, Cr, Fe, Zn.

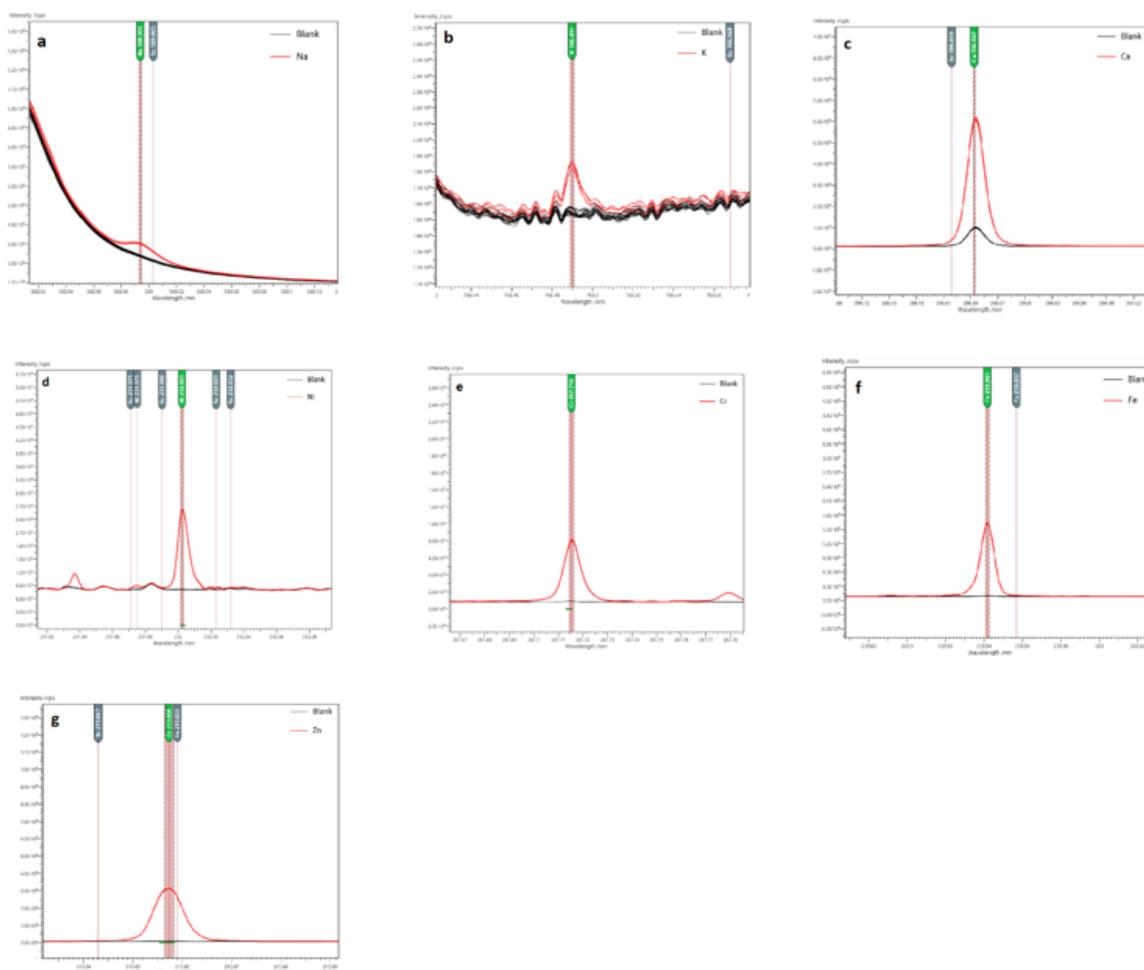


Figure 3. Spectrums in blank CED primer. a) Na spiked blank CED primer (0.60 mg/kg) b) K spiked blank CED primer (0.60 mg/kg) c) Ca spiked blank CED primer (0.60 mg/kg) d) Ni spiked blank CED primer (0.60 mg/kg) e) Cr spiked blank CED primer (0.60 mg/kg) f) Fe spiked blank CED primer (1.00 mg/kg) g) Zn spiked blank CED primer (1.00 mg/kg)

Generally, it is accepted that there are no interfering components if response is less than 20% of limit of quantification for each analyte. In the light of this information, selectivity parameter for Ca and Zn is acceptable, as shown in Table 6. Also, no response was observed in blank samples except Ca and Zn.

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Table 5. Peak heights of Ca and Zn in blank CED primer

	Ca		Zn	
	Height	% Height	Height	% Height
LOQ	6476000	-	308372	-
Blank-1	974016	15.0	7812	2.53
Blank-2	973783	15.0	7822	2.54
Blank-3	974021	15.0	7823	2.54
Blank-4	998246	15.4	7728	2.51
Blank-5	1008000	15.6	7829	2.54
Blank-6	1003000	15.5	7871	2.55

3.2.3. Dilution Integrity

In order to observe dilution effect, concentrations which above linear calibration ranges were chosen as 60.0 mg/kg for Na, Ca, K, Ni, Cr, 40.0 mg/kg for Fe, Zn and spiked to blank CED primer. It was diluted 20 times with dilution solvent for 5 parallels. Also, diluted samples were found to remain within calibration range. Table 5 shows that no significant effect were observed in dilution process.

Table 6. Dilution integrity data

	Concentrations Measured						
	60.0 mg/kg					40.0 mg/kg	
	Na	K	Ca	Ni	Cr	Fe	Zn
Dilution-1	60.9	61.2	63.8	63.3	61.0	40.3	40.9
Dilution-2	61.6	62.0	62.8	63.8	61.3	41.0	41.6
Dilution-3	62.5	62.0	63.4	64.4	62.2	41.2	41.8
Dilution-4	62.8	62.0	62.8	63.9	61.5	40.9	41.6
Dilution-5	61.9	61.8	62.7	63.7	61.6	41.1	41.7
SD	0.750	0.346	0.480	0.396	0.444	0.354	0.356
Mean	61.9	61.8	63.1	63.8	61.5	40.9	41.5
RSD* (%)	1.21	0.561	0.760	0.621	0.721	0.864	0.858
Bias** (%)	3.23	3.00	5.17	6.37	2.53	2.25	3.80

SD: Standart Deviation, RSD: Relative Standart Deviation
 * $[\text{SD}/\text{Mean}] \times 100$ ** $[(\text{measured concentration.}) - (\text{expected concentration.})]/(\text{expected concentration.}) \times 100$

3.2.4. Matrix Effect

Matrix effect was evaluated by spiking low (2.40 mg/kg Na, K, Ca, Ni, Cr, 4.00 mg/kg Fe, Zn and 2.00 mg/kg Sc) concentrations to six different blank CED primers and dilution solvent. Also, peak heights were compared as shown in Table 7. In consequence, analytes and internal standart were neither negatively nor positively affected by matrix effect.

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Table 7. Matrix effect data

	Peak Heights							
	2.40 mg/kg			4.00 mg/kg		2.00 mg/kg		
	Na	K	Ca	Ni	Cr	Fe	Zn	Sc
DS	463362	17964	19320000	77852	280448	646980	1265000	6049000
Blank-1	465595	18118	19540000	76953	275614	631453	1252000	5932000
Blank-2	460942	18046	18660000	75045	269359	637940	1237000	5585900
Blank-3	460941	18000	19200000	76000	270359	626085	1247000	5760000
Blank-4	460941	17968	19340000	77099	274008	633369	1249000	5894000
Blank-5	458558	17966	19760000	77277	276831	628409	1251000	5975000
Blank-6	464453	18156	19330000	76548	275195	636874	1251000	5933000
SD	2441.64	78.5948	339446	924.942	3793.46	69.7225	8260.64	154947
Mean	462105	18031	19307143	76682	274545	634444	1250286	5875557
RSD* (%)	0.528	0.436	1.76	1.21	1.38	1.10	0.661	2.64

DS: Dilution Solvent, SD: Standart Deviation, RSD: Relative Standart Deviation
 *[SD/Mean] x100

3.2.5. Linearity

For each analytes, a five-point calibration curve was drawn between 0.60-6.00 mg/kg for Na, K, Ca, Ni, Cr and 1.00-20.0 mg/kg for Fe, Zn. Linearity of the method was determined by measuring peak intensity ratios of all analytes spiked at different concentrations of dilution solvent. Linearity was calculated with regression coefficient (R^2) value. Calibration curves of all analytes are given in Figure 4.

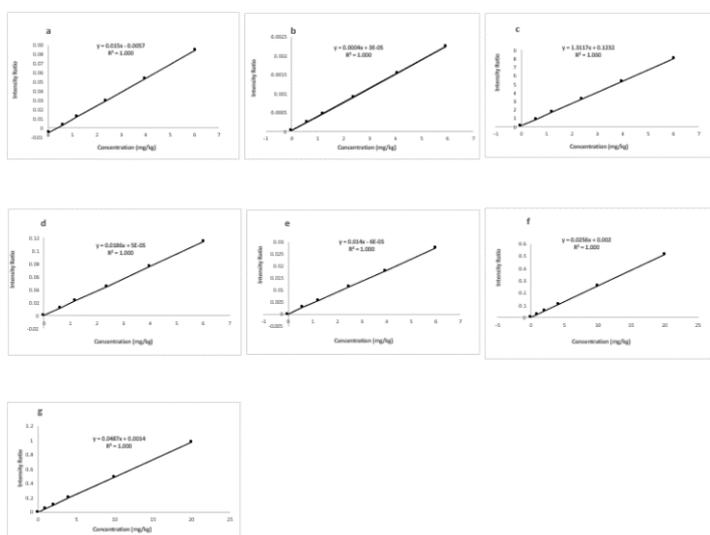


Figure 4. Calibration curves of all analytes a) Na (0.60-6.00 mg/kg) b) K (0.60-6.00 mg/kg) c) Ca (0.60-6.00 mg/kg) d) Ni (0.60-6.00 mg/kg) e) Cr (0.60-6.00 mg/kg) f) Fe (1.00-20.0 mg/kg) g) Zn (1.00-20.0 mg/kg)

3.2.6. Accuracy and Precision

Accuracy of the method was determined by analyzing the quality control samples for three days. Five parallel spiked CED blank samples of Na, K, Ca, Ni, Cr, Fe, Zn were monitored at each quality control concentration level to determine accuracy of the experiment (Na, K, Ca, Ni, Cr; 0.60 and 2.40 mg/kg, Fe, Zn; 1.00 and 4.00 mg/kg). Accuracy were found to be within acceptable ranges between 95.0% -113% for Na, K, Ca, Ni, Cr and 98.0%-105% for Fe, Zn. Two different concentration levels of spiked CED blank samples were injected on three different days to determine intraday and interday precision (Na, K, Ca, Ni, Cr; 0.60 and 2.40 mg/kg, Fe, Zn; 1.00 and 4.00 mg/kg). All results were summarized in Table 8.

Table 8. Intra-day and inter-day data

Spiked CED blank concentration/mg kg ⁻¹	Intra-day			Inter-day		
	Concentration measured (n=5)/mg kg ⁻¹ (mean±S.D.)	RSD.* (%)	Accuracy (%)	Concentration measured (n=18)/mg kg ⁻¹ (mean±S.D.)	RSD.* (%)	Accuracy (%)
Accuracy and precision for Na						
0.60	0.58±0.01	1.61	97.5	0.56±0.00	0.620	99.1
2.40	2.36±0.03	1.13	98.2	2.35±0.01	0.425	98.0
Accuracy and precision for K						
0.60	0.65±0.02	3.14	109	0.63±0.02	2.96	105
2.40	2.46±0.02	0.986	102	2.43±0.04	1.59	101
Accuracy and precision for Ca						
0.60	0.66±0.00	0.126	111	0.66±0.02	3.38	109
2.40	2.49±0.04	1.43	104	2.45±0.02	0.955	102
Accuracy and precision for Ni						
0.60	0.60±0.01	0.937	100	0.58±0.01	1.60	97.0
2.40	2.50±0.01	0.491	104	2.48±0.02	0.990	103
Accuracy and precision for Cr						
0.60	0.62±0.01	1.27	103	0.60±0.01	2.16	101
2.40	2.41±0.01	0.858	100	2.38±0.00	0.140	99.2
Accuracy and precision for Fe						
1.00	0.99±0.01	0.888	99.2	0.99±0.01	0.568	98.9
4.00	4.19±0.03	0.670	105	4.19±0.02	0.408	105
Accuracy and precision for Zn						
1.00	1.02±0.01	1.02	102	1.01±0.00	0.329	101
4.00	4.11±0.03	0.631	103	4.14±0.05	1.14	104

*[Standard deviation/mean concentration measured] x 100. S.D: Standart Deviation RSD: Relative Standart Deviation

3.2.7. Recovery

Efficiency of the extraction was performed by adding known quantities of all analytes to CED primer consisting of 80% deionized water, 15% binder (epoxy), 1% pigments, 2% fillers, 1% additives and 1% solvents. Recovery were found to be within acceptable range between 80.0%-120 % (LOQ concentration) and 85.0%-115 (low concentration) for all analytes. The results are shown in Table 9.

Table 9. Recovery results for CED primer consisting of 80% deionized water, 15% binder (epoxy), 1% pigments, 2% fillers, 1% additives and 1% solvents.

Analytes	Initial concentration (n=3)/mg kg ⁻¹ (mean±SD)	Added (mg kg ⁻¹)	Found (n=6)/mg kg ⁻¹ (mean±SD)	RSD* (%)	Recovery (%)
Na	0.43±0.02	0.60	0.98±0.01	1.20	91.2
		2.40	2.83±0.01	0.648	99.8
K	0.72±0.00	0.60	1.22±0.01	0.616	83.5
		2.40	3.05±0.00	1.02	97.1
Ca	0.64±0.00	0.60	1.22±0.00	1.67	97.0
		2.40	3.02±0.03	1.12	99.2
Ni	ND	0.60	0.61±0.01	0.741	102
		2.40	2.52±0.02	0.683	105
Cr	0.09±0.00	0.60	0.67±0.01	0.693	96.8
		2.40	2.43±0.01	0.547	97.6
Fe	2.69±0.01	1.00	3.75±0.02	0.459	106
		4.00	6.79±0.04	0.621	103
Zn	17.2±0.01	1.00	18.3±0.07	0.380	110
		4.00	21.3±0.04	0.192	102

*[Standard deviation/mean concentration measured] x 100. S.D: Standart Deviation RSD: Relative Standart Deviation

4. Conclusion

Within the scope of this study, rapid and robust liquid-liquid extraction method was developed to determination of Na, K, Ca, Ni, Cr, Fe, Zn in CED primer consisting of 80% deionized water, 15% binder (epoxy), 1% pigments, 2% fillers, 1% additives, 1% solvents and analyzed by ICP-OES system. The validity of this method was performed by Eurachem Guideline [17]. Neither of these elements has ever been analyzed simultaneously in CED primer by using ICP-OES. The proposed method provides sensitive, rapid, accurate and precise analysis of the mentioned elements in CED primers for coating companies and their customers to prevent coating defects. Moreover, this study is expected to have an impact on quality control in the paint industry.

Ethics in Publishing

There are no ethical issues regarding the publication of this study.

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