

Solid Phase Extraction of Co(II) Using Activated Carbon Obtained from Grape Stalk Prior to High-Resolution Continuum Source Flame Atomic Absorption Spectrometric Detection

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ABSTRACT: In this study, a new Solid Phase Extraction (SPE) method was developed for the detection of cobalt ions in water and food samples with High-Resolution Continuum Source Flame Atomic Absorption Spectroscopy (HR-CS FAAS). Cobalt ions were recovered and separated for the first time using grape stalk-based active carbon in this work (ACGS). Separation and preconcentration operations were carried out using the column method. Sample solution pH, eluent type and concentration, flow rates of the sample solution and eluent, sample solution volume, the influence of foreign ions, and adsorbent capacities were tested to find the best conditions for the recovery of analyte ions. The pH was set to 7.0, the extraction eluent volume was 5 mL 2 mol/L, and the sample flow rate was 4 mL/min in order to produce the best extraction possible. Under optimum conditions, the Limits of Detection (LOD) and Relative Standard Deviation (RSD) were obtained as 0.27 µg/L and 2.3%, respectively, and the maximum adsorption capacity based on the Langmuir was found to be 8.1 mg/g. Analyte ions were added to real samples to test the method's accuracy, and the results were then compared to those of other methods and reference materials (SRM). More than a few water and food samples were successfully tested this way.

KEYWORDS: Cobalt; solid phase extraction; activated carbon; grape stalk; Atomic Absorption Spectrometry.

INTRODUCTION

The consequences of trace elements on live beings can be considerable. Some of them are essential for life, but excessive use might have detrimental effects [1,2]. Some chemicals require suitable quantities of cobalt in order to function properly [3]. Red blood cell formation and anemia prevention are critical functions of vitamin B12, which contains cobalt [4]. Cobalt is carcinogenic at

high levels, yet the human body needs around 1 mg of it to function properly [5]. Drinking water typically has cobalt amounts of <1–2 µg/L. Regarding cobalt exposure, food is one of the most common culprits. Metals such as cobalt contained in inorganic wastewater from industries tend to accumulate in the food chain. Heavy metals are highly absorbable by living organisms

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due to their high solubility in the aquatic environment. The estimated dietary intake of cobalt is between 5 to 40 micrograms per day, and most of this is inorganic cobalt [6,7]. Cobalt can cause thyroid damage, impaired lung function, vomiting, diarrhea, elevated blood pressure, and delayed breathing when ingested in large doses. It is crucial for human health, then, that cobalt be removed from our drinking water, food, and other environmental samples [8]. Samples containing cobalt ions often fall below the detection threshold of most equipment. Cobalt in a complicated matrix context is difficult to analyze using these methods [9]. As a result, precise analytical procedures are required [10].

Metal ions in water, environmental samples, and food samples can be detected using various preconcentration and separation techniques, including co-precipitation [11], Cloud Point Extraction (CPE) [12-14], ion exchange [15], Liquid-Liquid MicroExtraction (LLME) [16], Dispersive Liquid-Liquid MicroExtraction (DLLME) [17,18], Solid Phase Extraction (SPE) [19-21], and Dispersive Micro-Solid Phase Extraction (DMSPE) [20,22].

SPE is a preconcentration technique that uses analyte accumulation on a solid surface. You have the option to enhance or eliminate the species you find using this strategy. Simple, quick, and inexpensive, SPE preconcentration is one of the most successful preconcentration technologies available. It also has a high preconcentration factor. For many metal ions, SPE has become the method of choice for enrichment prior to analysis by FAAS and other techniques. Due to its low cost, ease of use, and high sample yield, FAAS is widely used for detecting metal ions in various samples [3,14,20,23,24]. It is the primary goal of preconcentration and/or separation to separate and remove trace metals from their complex sample surroundings into a known environment and to detect them sensitively in an environment that does not involve any attempt to detect them through transformation. Separating trace metals from their major and minor components, as well as arranging them in smaller amounts, guarantees that the concentrations of these elements reach the detection limit. The lower Limit of Detection (LOD) can be reduced in this way, making the approach more sensitive [25]. SPE relies heavily on the sorbent. Analytical methods have undergone a great deal of research to improve their properties. SPE investigations with nanoporous-Activated Carbon (AC) are ongoing [26].

Controlling the pyrolysis and thermal activation of raw materials with significant carbonic storage, such as fruit peels or seeds, results in the production of active carbon [27]. It is possible to create numerous types of activated carbons with varying porous structures, strong chemical stabilities, high adsorption capacities, and tunable pore diameters [28]. These activated carbons have been selected as flexible adsorbents for gaseous and water-soluble contaminants. Additionally, their extensive usage as adsorbents includes the elimination of undesirable color, flavor, taste, and organic pollutants as well as other inorganic contaminants from industrial effluent, the management of air pollution, and the recovery of solvent from settlements. In the pharmaceutical business, AC is increasingly favored for use in treating bacterial infections in some illnesses and eliminating toxins from the human body, and coloring syrups. Otherwise, they are used in hydrometallurgical industries as catalysts, catalyst support materials, and for the recovery of silver, gold, and other metals. Additionally, AC is employed in the chemical, food, and gas mask filter manufacturing industries. It is also well known for its use in vehicle pollution control devices [29,30]. Although numerous kinds of carbonaceous materials can be used for making activated carbon [28]. The most important factor is that the substance to be used in activated carbon is accessible, plentiful, and cheap. Therefore, increased attention has been aimed at finding affordable and unconventional precursors, such as agricultural and industrial wastes, for the production of efficiently activated carbons. Among the preconcentration and separation methods, AC has advantages. These are (i) high preconcentration factor; (ii) ease of automation; (iii) ease of use; (iv) reusability of the adsorbent; (v) low reagent consumption. With SPE applications, apart from separating and preconcentrating the samples, it is also possible to obtain samples with known content similar to calibration solutions [30,31].

Using High-Resolution Continuum Source Flame Atomic Absorption Spectroscopy (HR-CS FAAS) to detect cobalt ions in water and food samples, this study developed a new SPE method. In this study, for the first time, cobalt ions were recovered and separated utilizing grape stalk-based active carbon (ACGS). During preconcentration operations using the column approach, variables such as sample solution pH, eluent type and concentration, solution flow rate, sample solution volume and adsorbent

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Table 1: HR-CS FAAS conditions for Cobalt measurement.

Parameters	Value
Wavelength, nm	240.72
The flow rate of C ₂ H ₂ -air, L/h	60
Burner height, mm	6
Evaluation Pixels, pm	3
Background correction	Simultaneous

quantity were examined. Optimized adsorption conditions for the analyte on ACGS were found. After identifying the most favorable circumstances, cobalt ions were preconcentrated and detected in various real samples. Accuracy, precision and validity of detection were confirmed using known methods and standard reference material. There are studies about the use of AC in the literature [30-34]. Few studies have been found in the literature on the activated carbon used in the study. Additionally, it is an environmentalist study that also provides an economic evaluation of agricultural wastes that a new separation and determination method has been developed for the determination and preconcentration of cobalt ions.

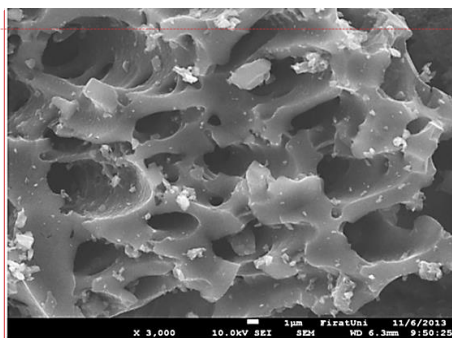
EXPERIMENTAL SECTION

Reagents and standard solutions

All the chemicals and reactive used in the studies were of high purity and analytical grade. All the chemicals were purchased from Merck Company (Darmstadt, Germany). All aqueous solutions were made with ultrapure water from a Milli-Q water treatment system (resistivity = 18.3 MΩ/cm) (Millipore, Corporation, MA, USA). We bought standard stock solutions (1000 mg/L) from Merck Co. (Darmstadt, Germany). Daily preparation of the study solutions involved the proper dilution of the stock solutions. NIST SRM 1640a, a certified reference item, was used throughout the experimental experiments (trace elements in water).

Instrumentation

We used an Analytik Jena ContrAA 300 Model HR-CS FAAS from GLE in Berlin for our metal detection. Cobalt ions were atomized using an air-acetylene (C₂H₂) combination flame. For the best analyte signal, device parameters were set according to the catalog values for flame composition and flame head height. Table 1 lists the operating parameters for cobalt in the HR-CS FAAS.

**Fig. 1: SEM micrographs of activated carbon [35]**

A HANNA brand HI 2211 digital pH meter (Europe/Romania) was used to obtain pH readings. An ISMATEC REGLO peristaltic pump was used to regulate the flow rate.

Separation column preparation

Erdem *et al.* synthesized the active carbon derived from grape stalk (ACGS) used in this work [35]. The activated carbon obtained from the grape stalk used was subjected to chemical activation (ZnCl₂) and the carbonization process was started. The surface properties, pore distribution and structural properties of the obtained activated carbon were clarified by character analyses such as XRD, FT-IR, SEM, BET and TGA. In the SEM image of the ACGS shown in Fig. 1, channels, cavities, and massive exterior surface cracks have high adsorption features due to the appropriate pore size, large surface area, and extremely porous structure. According to the characterization results, the BET surface area, pHzpc, total pore volume, and the yield of activated carbon prepared under optimum conditions were determined as 1411 m²/g, 2.84 and 0.723 cm³/g, respectively. Additionally, to determine the adsorption property of activated carbon on the surface, the iodine number was determined as 1760 mg/g [35].

Glass columns with a length of 15 cm and a diameter of 10 mm, equipped with a stopcock and a capacity of 250 mL were used. Impurities were eliminated and the weight of the active carbon (0.1-0.6 g ACGS) was fixed before it was deposited in columns with glass wool at the bottom. Glass wool was also placed on the top of the column fill material to prevent it from being damaged and distributed by solution flow. When the column was first prepared for use, it was washed twice with

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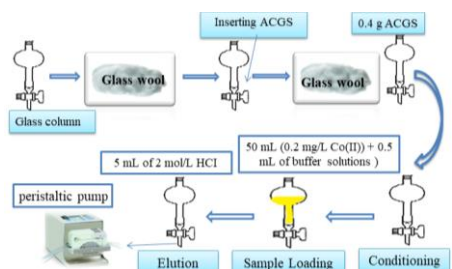


Fig. 2: Diagram of the SPE method.

two different acid solutions, one with 2 mol/L HCl and one with 2 mol/L HNO₃, as well as water, and then conditioned with a blank solution at an empirically established pH value. A peristaltic pump was used to deliver the model solutions across the column, the species were detected by inserting an HR-CS FAAS into a suitable recovery solution and then washing the column with 10 mL distilled water.

Extraction/preconcentration procedure

Following the study's aims, it was established that ACGS generated may be used to preconcentrate Co(II) ions. Sample solution pH, eluent type and concentration, flow rates of the sample solution and eluent, sample solution volume, the influence of foreign ions on the recovery yield of analyte ions, and adsorbent capacities were tested to find the best conditions for the recovery of analyte ions. Separation and preconcentration operations were carried out using the column technique. With the column technique, the most appropriate experimental conditions were identified using a 50 mL model solution containing 10 µg Co(II) for solid phase extraction of Co(II) ions. The adsorbent was conditioned by treatment with a blank solution set to the most appropriate pH value determined experimentally and later, a peristaltic pump was used to move the model solution through the column. The cobalt ions adsorbed on ACGS were separated with 3 mL/min flow rate of 5 mL 2 mol/L HCl eluent solution. Eluents were analyzed with HR-CS FAAS for the determination of metal concentrations. The diagram of the developed SPE method is shown in Fig. 2.

Sample preparation

Tap water was obtained from the research facility of Ahi Evran University and various locations throughout

the city. River water was procured from the Kizilirmak River, while geothermal water was procured from Terme in the province of Kirsehir. Water samples were run through membrane filters with a pore size of 0.45 µm (Millipore). Certain amounts of water samples taken at appropriate volumes for the measured containers had buffer solution (0.50 mL of 0.1 mol/L phosphate buffer solution (pH 7.0)) at amounts to ensure study pH values and known amounts of analyte added.

The food samples (black tea and rice) were taken from Kirsehir markets, they were washed with tap water and then deionized distilled water, then dried in an oven at 50 °C for 48 h before being ground in a mortar to powder. The food samples were digested by the wet acid digestion method. 0.5 g of each sample was taken in a beaker separately and then, added to 20 mL nitric acid (65% HNO₃, w/w) and 1 mL hydrogen peroxide (30% H₂O₂ w/w), respectively. The mixture was heated until dryness (until they evaporate into solutions) on a hot plate (~100 °C). The resulting gel-like layers were diluted with ultrapure water [3]. Analyses of the obtained mixtures were completed by applying the steps of the preconcentration method in the most appropriate conditions determined.

RESULTS AND DISCUSSION

Preconcentration parameters' optimization

Analyte ions can be recovered in the preconcentration columns constructed for this investigation under the following parameters and performance factors. There were three separate examinations of every sample in our investigation. The method's accuracy was tested using recovery tests in which analyte ions were added to genuine samples and certified standard reference material, and the procedure was applied to real samples.

Effect of pH

The sample solution pH has a major impact on extraction efficiency [36]. The column was filled with model solutions of various pH values and flowed at the optimum rate. It was possible to plot the recovery yield percentage for analyte ions as a function of solution pH. The pH value provides an acceptable recovery yield (between 95 and 105%) for analytical purposes was assessed as the most suitable pH value. As given in Fig. 3, the highest recovery rates (>95%) were found at pH 7.0. With further increase in pH, extraction recovery

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Table 2: Eluent solution's effect on the recovery of cobalt ions (sample volume: 50 mL, pH: 7.0, flow rate of sample: 4 mL/min, flow rate of eluent: 3.0 mL/min, adsorbent: 400 mg, N=3).

Eluent	Recovery (%)
1 mol/L HCl, 5 mL	88±4
2 mol/L HCl, 5 mL	97±3
3 mol/L HCl, 5 mL	94±3
1 mol/L HNO ₃ , 5 mL	85±3
2 mol/L HNO ₃ , 5 mL	87±2
3 mol/L HNO ₃ , 5 mL	84±2
1 mol/L HCl, 1 mol/L HNO ₃ (1/1: v/v) 5 mL	90±3
2 mol/L HCl, 2 mol/L HNO ₃ (1/1: v/v) 5 mL	95±2

* Results are mean ± standard deviation of three replicate analyses

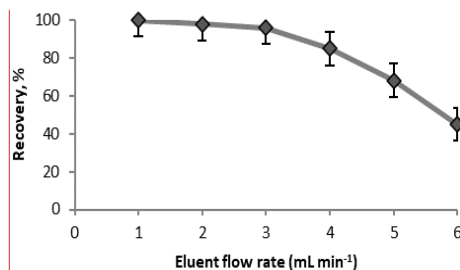


Fig. 4: Effect of the flow rate of eluent solution on the recovery of cobalt ions (sample volume: 50 mL, pH: 7.0, eluent: 2 mol/L HCl, flow rate of sample: 4 mL/min, adsorbent: 400 mg, N=3).

Fig. 3: Effect of the pH of the sample solution on the recovery of cobalt ions (sample volume: 50 mL, eluent: 2 mol/L HCl, flow rate of sample: 4 mL/min, adsorbent: 400 mg, N=3).

was reduced, possibly due to the formation of cobalt hydroxide. Accordingly, pH 7.0 was chosen for the analysis of cobalt ions in later studies and real samples. The amount of buffer was also optimized by adding 0.50, 1.0, 1.5, and 2.0 mL of buffer solution. There was no significant change observed in the recovery values using different amounts of buffer. 0.5 mL volume of buffer was selected considering the lower standard deviation. Hence, all further studies were conducted at pH 7.0 using 0.50 mL of 0.1 mol/L phosphate buffer solution.

Concentration and eluent kind effect

Full desorption of the adsorbed analyte is an important characteristic that affects recovery yield in preconcentration investigations with SPE. Analyte desorption is critical for precise detection and for increasing the method's sensitivity. Acids, bases, or organic solvents are commonly used as eluent solutions in scientific experiments [19,36].

To discover the best eluent in this study, numerous inorganic acids and their combinations, which are routinely employed, were tested at optimal circumstances. The optimal conditions for the removal of cobalt ions from ACGS were examined using various acid solutions and combinations. Table 2 summarizes the findings.

Desorption of Co (II) from the surface of the adsorbent was achieved by using a dilute solution of mineral acids like HCl and HNO₃. Therefore, for quantitative recovery of Co(II) ions, the adsorption studies were conducted by using 1–3 mol/L of HCl and HNO₃ solutions. A small volume of eluent solution is required to obtain a high preconcentration factor. In some cases, the small eluent solution volume may not be sufficient to recover the elements adsorbed in the column. In such cases, if the column is not affected by high acid or base concentration, the concentration of the eluent solution can be increased. The highest recovery value was recorded with 2.0 M HCl solution. As shown in Table 2, a decrease in the recovery values was observed after 2.0 M. Results are given in Table 2 indicate that quantitative recovery (>95 %) Co(II) can be achieved using 5 mL of 2 mol/L HCl.

Effects of eluent and sample flow rates

Under the most suited experimental circumstances, the flow rate of eluent and sample was studied to see how it affected the recovery yield of cobalt ions (pH, eluent type, etc.). In to obtain maximum recoveries for cobalt, different sample and eluent flow rates were tested at optimum conditions. As shown in Fig. 4, it was found that the suitable value for the flow rate of the eluent solution was in the range of 1–3 mL/min. Therefore, an optimum flow

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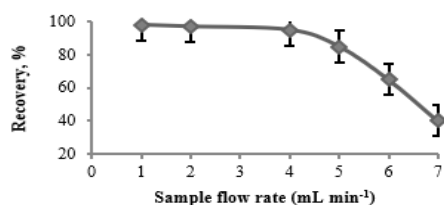


Fig. 5: Effect of sample solution flow rate on cobalt ion recovery (sample volume: 50 mL, pH: 7.0, eluent: 2 mol/L HCl, the flow rate of eluent: 3.0 mL/min, adsorbent: 400 mg, N=3)

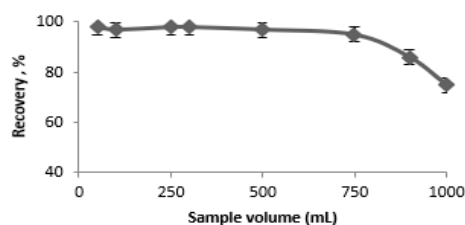


Fig. 6: Effect of sample volume on the recovery of cobalt ions (pH: 7.0, flow rate of sample: 4 mL/min, eluent: 2 mol/L HCl, flow rate of eluent: 3.0 mL/min, adsorbent: 400 mg, N=3).

rate of 3 mL/min was selected as the eluent solution flow rate to decrease the analysis time.

The model solutions containing Co(II) were passed through the column at flow rates of 1-7 mL/min. The most appropriate flow rate was found to be 4 mL/min (recovery yield >95%) (Fig. 5). At a higher flow rate the recovery yield was reduced. Later experiments used a sample flow rate of 4 mL/min.

Effect of sample volume

The final volume of the sample solution determines the preconcentration factor, and the extraction efficiency of the developed method. In order to calculate the preconcentration factor, sample volumes corresponding to 95% and more analytically of the recovery of cobalt ions need to be found. The sample volume was increased while maintaining the amount of the detected element constant in order to determine the maximum solution sample volume that may be used. The column was used to pass through 50-1000 mL solution mixtures containing 10 µg Co(II) at the most suited circumstances (pH, flow rate, etc.). The preconcentration factor (PF) was calculated as the ratio of the largest sample volume to the eluent volume

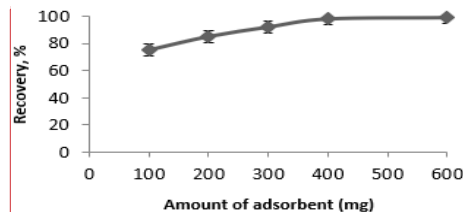


Fig. 7: Effect of sorbent amount on the recovery of cobalt ions (sample volume: 50 mL, pH: 7.0, eluent: 2 mol/L HCl, the flow rate of eluent: 3.0 mL/min, the flow rate of sample: 4 mL/min, N=3).

that was most suited. Experiments showed that 750 mL was the optimal sample volume for quantitative recovery (recovery >95 %) (Fig. 6). Analytical ions were recovered with an adequate volume of 5 mL eluent, and the theoretical preconcentration factor was computed as 150 (750 mL of sample/5 mL of eluent).

Effect of amounts of ACGS

The effects of the amount of ACGS on the sorption of metal ions at optimum conditions (pH, flow rate, eluent, etc.) were in the range of 100-600 mg. As seen in Fig. 7, quantitative recoveries (recovery >95 %) were obtained in the range of 400-600 mg. Therefore, 400 mg ACGS was selected for further studies.

Effect of foreign ions

The most important stage in chemical analysis is the determination of whether the sample medium (matrix) has a degrading effect on the analyte or not. In methods developed with this aim, the effect of foreign ion interactions on the recovery yield of analyte ions was researched by adding different concentrations of various cations and anions to the model solutions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Cu^{2+} , Pb^{2+} , Ni^{2+} , Cd^{2+} , Cr^{3+} , Fe^{3+} , Cl^- , SO_4^{2-} , CO_3^{2-}). The recovery yield of analyte ions was estimated using model solutions with varying amounts of foreign ions that were run through the column (Table 3).

These recovery values showed that normally present ions in water and food samples have no significant interference on the extraction and determination of cobalt in sample solutions. The Co(II) ions were almost quantitatively recovered in the presence of the interfering ions.

Capacity of the ACGS and adsorption models

It is critical to determine the adsorbent capacities to assess

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Table 3: Effects of some foreign ions on the recovery of cobalt ions (sample volume: 50 mL, pH: 7.0, flow rate of sample: 4 mL/min, eluent: 2 mol/L HCl, flow rate of eluent: 3.0 mL/min, adsorbent: 400 mg, N=3).

Foreign ions	Concentration (mg/L)	Recovery (%) Co ²⁺
K ⁺	1000	95±2
Na ⁺	2000	94±1
Ca ²⁺	500	96±2
Mg ²⁺	200	95±2
Cl ⁻	100	101±4
	500	96±2
SO ₄ ²⁻	25	97±3
	50	95±2
CO ₃ ²⁻	250	97±3
	500	99±4
Zn ²⁺	10	95±1
Cu ²⁺	10	96±2
Pb ²⁺	10	94±1
Ni ²⁺	10	95±2
Cd ²⁺	10	97±1
Cr ³⁺	10	96±2
	10	97±2
Fe ³⁺	10	97±2
	50	[102±3]

* Results are mean ± standard deviation of three replicate analyses.

the degree to which the amounts of species found in a medium can be adsorbed by an adsorbent. The adsorption capacity of ACGS was determined by the batch method. Under the most favorable conditions determined for this purpose, 100-400 mg adsorbent was added to 100 mL model solutions containing analyte ions at various concentrations (pH 7.0). The mixtures were mixed at room temperature at 150 rpm for 2 h [34]. Later 5-10 mL was taken from these solutions and analyzed with HR- CS FAAS after the necessary dilutions.

The Langmuir adsorption model was used to define the equilibrium isotherm in order to explore the adsorption type. For the Langmuir model, Eq. (1) represents the linearized equation form, which was employed in this work to determine the maximal metal uptake.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + C_e \left(\frac{1}{Q_0} \right) \quad (\text{linear form}) \quad (1)$$

According to the above equation, C_e is the analyte concentration in the solution at equilibrium (mg/L), q_e is the analyte amount adsorbed per unit adsorbent

Table 4: Adsorption capacities of Co²⁺ by various AC

Adsorbent	Q _{max} (mg/g)	Refs.
HSAC ^a	13.88	[31]
ASAC ^b	111.11	[32]
AC ^c	1.2	[11]
PoP400 ^d	373	[34]
PoP600 ^e	405	
PBNP ^f	7.41	[30]
ACGS	8.1	This work

HSAC^a: Activated carbons generated from hazelnut shells

ASAC^b: Activated carbon from Apricot stone

AC^c: Activated carbon

PoP400^d, PoP600^e: Activated carbons from potato peels,

PBNP^f: Activated charcoal modified with Prussian blue NPs

at equilibrium (mg/g), Q₀ is the maximum adsorption capacity (mg/g), and K_L is a constant representing adsorption energy. To be able to calculate the Langmuir constants, the graph of C_e/q_e values against C_e was drawn. In the Langmuir isotherm, the slope is 1/Q₀, while the intersection is 1/K_LQ₀, and the Langmuir constants are calculated from the common solution to these equations [37,38].

The Langmuir model was shown to fit the experimental data well, with a correlation coefficient (R²) of 0.990. The Langmuir monolayer adsorption capacity (Q₀) and b were estimated as 8.1 mg/g and 0.136 L/g, respectively. According to the Langmuir model, the adsorption of cobalt on ACGS occurs in a single layer on the surface, and the R² value of 0.990 confirms that this is the case [37]. A comparison of various AC's adsorption capacities is shown in Table 4.

The maximum adsorption capacities of treated AC for the Co were compared in terms of optimal conditions, and adsorption patterns with different types of adsorbents which have been reported and documented in the scientific literature as shown in Table 4. Unlike other adsorbents, the AC material can be considered a cost-effective and fast alternative: some adsorbents might have higher adsorption power, but their adsorption process takes a long time. Besides, due to its good adsorption capacities obtained, AC is a promising adsorbent for treating cationic Co, which is known for the difficulty of its removal from aqueous solutions.

Analytical performance

Table 5 lists the analytical performance parameters

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Table 5: Analytical performance and optimum conditions of the proposed method for the determination of cobalt ions.

Parameters	Co ²⁺
pH	7.0
Amount of activated carbon (mg)	400
Eluent volume (2 mol/L HCl)	5
Eluent flow rate (mL/min)	3
Sample flow rate (mL/min)	4
Maximum sample volume (mL)	750
Precision (RSD, N=7) (%)	2.3
Mean Recovery ^a (R%, $R \pm ts/\sqrt{N}$) N=7	97±1
Detection limit (LOD, µg/L)	0.27
Quantification limit (LOQ, µg/L)	0.9

^a Mean recovery at a 95% confidence level

for the suggested approach that were discovered under ideal circumstances. The linear interval of the graph, the equation for the calibration graph, the Limit of Detection (LOD), Limit of Quantification (LOQ), and relative standard deviation for repeated measures (%RSD) were identified under the most suitable experimental conditions. Various model solutions (7) generated with the same volume and concentration underwent preconcentration in the most suitable conditions to test the method's accuracy and determine the mean recovery yield (percent) and Relative Standard Deviation (%RSD) for repeated measurements. The LOD and LOQ values were calculated by 3 and 10 times the standard deviation values for measurements of blank solutions (N=15) with the following equations [$3s_b/m$] and [$10s_b/m$]. Here, m is the slope of the calibration curve and s_b is the standard deviation of the blank signals. The LOD and RSD % were obtained as 0.27 µg/L and 2.3%, respectively. The calibration curves were observed as linear and the concentrations range from 0.2-4.0 µg/mL with a correlation coefficient $R^2 = 0.9954$. The Enrichment Factor (EF) was calculated from the ratio of slope from the SPE method/Slope from normal HR-CS FAAS [19]. EF was 145. The extraction efficiency % calculated from $(EF/PF) \times 100$ is 97.

The accuracy of the method was tested with recovery experiments completed with the addition of analyte with known amounts to real samples and using standard reference material NIST SRM 1640a (Trace Elements in Natural Water) with Co content of 20.24±0.24 µg/kg. The result is based on the mean of three repeats using

Table 6: The Determination of cobalt ions in water samples (N=3).

Sample	Added (µg/L)	Found ^a (µg/L)	Recovery, %
Tap water	0	3.2±0.5	96
	5.0	8.0±0.6	
River water	0	1.6±0.3	104.0
	5.0	6.8±0.6	
Geothermal water	0	1.85±0.08	95.5
	10	11.4±1.2	

^a Mean±standard deviation.

Table 7: The Determination of cobalt ions in food samples (N=3).

Sample	Added (µg/g)	Found (µg/g)	Recovery, %
Black tea	0	BDL ^a	-
	1.5	1.54±0.06 ^b	102.7
	2.5	2.56±0.18	102.4
Rice	0	0.452±0.021	-
	1.5	2.01±0.10	103.8
	3.0	3.34±0.15	96.3

^a Below detection limit.

^b Mean±standard deviation.

the suggested method, the content of Co determined in this SRM was 19.28±0.17 µg/kg and results showed (Recovery, 95.2 %) good compatibility with the certified values.

Detection of cobalt ions in real samples

The developed separation/preconcentration method was applied with the aim of detecting Co(II) levels in city mains water, river water, and geothermal water and food samples (black tea and rice). The accuracy of the method was tested with recovery studies completed by adding known amounts of analyte ions to real samples (Tables 6 and 7). Satisfactory agreements were obtained between the added and detected levels of analytes for all samples. These values show that the developed method is suitable for the determination of trace amounts of cobalt (II) ions in different samples.

Comparison of the method with other

With SPE applications, apart from separating and concentrating the samples, it is also possible to obtain samples with known content similar to calibration solutions. Table 8 summarizes a comparison of the suggested method for detecting Co (II) with various known preconcentration and separation methods [10,14,17,20-22,39]. When compared with the studies in the literature,

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2. % Recovery calculations have been checked. Calculations have been verified.

Table 8: Comparison of some analytical performance variables determined with some analytical performance variables in the literature.

Method	LOD ^a µg/L	RSD ^b %	PF ^c	Linear Range µg/L	Recovery (%)	Sample	References
CPE-FAAS	1.0	3.6	25	250-5000		Water and Food	[14]
DLLME-SQT-FAAS	4.7	2.5	-	10-250		Biological fluids	[17]
dSPE-SQT-FAAS	4.6	3.3	61.5	15-150		Biological fluids	[20]
SPE-FAAS	4.4	-	10	500-4000		Fruit Samples	[21]
DMSPE/EDXRF	0.33	2.7	2242	-	97	Water	[22]
SPE-FAAS	0.24	1.8	200	200-5000	98.4	Water	[39]
SPE-FAAS	12.3	1.3	200	40-450		Water	[40]
ISSFME-FAAS	0.8	2.3	50	2-100		Water and Food	[41]
SPE-FAAS	0.27	2.3	150	200-4000	97	Water and Food	Current paper

^a Limit of detection^b Relative standard deviation^c Preconcentration factor, DMSPE: Dispersive micro-solid phase extraction, dSPE: dispersive solid phase extraction, ISSFME: situ sorbent formation microextraction, DLLME: Dispersive liquid-liquid microextraction, CPE: Cloud point extraction, SQT: Slotted quartz tube

the proposed method has a lower detection limit, no additives are needed during the proposed extraction process and the activated carbon is prepared with a simple method using natural products. Additionally, it shows that ACGS is a repeatable and low-cost technique that can be used for the pre-concentration of cobalt ions in water and food samples.

CONCLUSIONS

For trace cobalt ions in certain water and food samples, an SPE-based column technique-based separation and preconcentration method was developed in this study. As a solid phase support material, ACGS was employed so that Co(II) ions can be determined in different samples, almost all of the Co(II) ions were adsorbed with only 400 mg adsorbent without using any organic complexing agents. Research and optimization were done on the experimental variables impacting the extraction yield of the method. The adsorbent remained steady after more than 75 cycles. Recovery tests were carried out to assess the accuracy of the proposed method, with satisfactory recoveries of 95-104% observed, confirming that the technique is accurate and free from matrix effects. The technique was used effectively to find cobalt ions in various water and food samples. Although it is a routine SPE method used, it is advantageous and an environmentalist study that also provides an economic evaluation of agricultural wastes. The created approach can be used to find Co(II) in various food and environmental samples, including soil and plants. The active carbon's surface may

be altered in the future, and experiments including the altered adsorbent may be attempted. Research might be done on the commercial active carbon potential of ACGS.

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