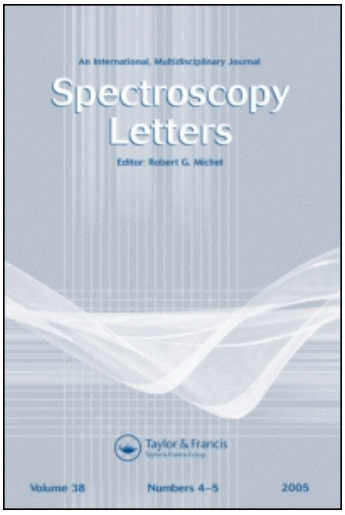

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Preconcentration of Platinum by Online Sorption for Graphite Furnace Atomic Absorption Spectrometry and Inductively Coupled Plasma Atomic Emission Spectrometry: A Comparative Study

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Abstract: A flow injection (FI) system was used to develop an efficient online sorption preconcentration system for graphite furnace atomic absorption spectrometry (GF-AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The investigated metal was preconcentrated on a microcolumn packed with 1,5-bis(2-pyridyl)-3-sulfophenyl methylene thiocarbono-hydrazide (PSTH) immobilized on an anion-exchange resin (Dowex 1 × 8-200) and placed in the autosampler arm for GF-AAS or in the injection valve of a FI manifold for ICP-AES. The metal was eluted from the column using a solution of 2 M HNO_3. Various parameters and chemical variables affecting the preconcentration and determination of platinum by GF-AAS and ICP-AES were evaluated. Under the optimum conditions, the usefulness of two different methods was studied and compared. The proposed FI-GF-AAS method has a detection limit of 1 ng mL^{-1}, and the precision of the method (RDS) was 1.6% at the 10 ng mL^{-1} level of Pt(IV); in the same way, the proposed FI-ICP-AES method has

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a detection limit of 7.4 ng mL^{-1}, and the precision of the method (RSD) was 3.06% at the 50 ng mL^{-1} level of Pt(IV).

Keywords: Environment, flow injection, GF-AAS, ICP-AES, platinum, preconcentration

INTRODUCTION

The emission of platinum group elements (PGEs), especially platinum, into the environment has increased during the past decade. This phenomenon has been commonly connected to the use of platinum in catalytic converters and has led to an increase of platinum and other PGEs in several natural matrices near intensive traffic lines.[1,2] The introduction of three-way catalyst has reduced the emissions of carbon monoxide (CO), unburned hydrocarbons (HC), and nitrogen oxides (NO_x) by 90%.[3] PGEs are the active components of these catalysts: Pt and Pd oxidizing CO to CO_2 and HC to CO_2 and H_2O, and Rh reducing NO_x. A clear link has been established between the increasing use of automobile catalysts and increasing environmental PGEs concentrations.[4–7]

The determination of platinum traces in environmental matrices requires highly sensitive analytical methodology. Different preconcentration/separation procedures have been developed and applied to the determination of Pt by AAS, ICP-AES, and ICP-MS techniques. Of all preconcentration and separation procedures, sorption possesses several advantages: large preconcentration factors that can be obtained in a short time, simplicity of phase separation, and suitability for automation. Column-based sorption techniques are frequently applied for the separation and preconcentration in flow injection atomic spectroscopy, first of all with AAS and ICP-AES, but also with AFS and ICP-MS. Numerous reviews devoted to PGEs determination have been published in the past decade.[8–16]

GF-AAS is a well-established technique with excellent sensitivity, and the equipment is available in many laboratories. Generally, the most robust commercially available GF-AAS instruments offer the possibilities for stabilized temperature platform furnace (STPF) conditions and Zeeman-effect background correction in connection with a transversally heated graphite atomizer (THGA). GF-AAS systems based on this concept provide higher and more homogeneous temperature conditions in the atom reservoir for the vaporation/atomization of PGEs and a less intensive extent of interferences.

ICP-AES methods are characterized by lower sensitivity to nonspectral interferences, but the large number of transition metals present as main constituents in environmental matrices can cause spectral interferences with the determination of PGEs. These effects, however, can be successfully overcome by the selection of alternative analytical lines and/or matrix separation.[17–19]

The purpose of this work was to develop and to compare two simple, sensitive, and selective FI online preconcentration and separation GF-AAS and ICP-AES methods for the determination of trace amounts of Pt in diverse samples. To reach this goal, we used a microcolumn packed with 1,5-bis(2-pyridyl)-3-sulfophenyl methylene thiocarbono-hydrazide (PSTH) immobilized on an anion-exchange resin (Dowex 1 × 8–200, Aldrich).

MATERIALS AND METHODS

Instrumentation

A Perkin-Elmer Zeeman/4100 ZL atomic absorption spectrometer equipped with a Perkin-Elmer AS-70 furnace autosampler was used throughout. Pyrolytic graphite-coated tubes with pyrolytic graphite platforms were used in all experiments. The primary radiation source was a platinum hollow cathode lamp operated at 15 mA; the selected wavelength was 265.9 nm with a spectral slit width of 0.7 nm. The peak area was taken as the signal measurement. The graphite furnace temperature program for the determination of platinum is shown in Table 1.

The ICP-AES system used was a Perkin-Elmer 40 sequential emission spectrometer equipped with a Perkin-Elmer AS-90 autosampler and controlled by an IBM XT-486 personal computer. The spectrometer output was connected to a PE Nelson Model 1020 personal integrator. Samples were Introduced via a Gem Tip cross-flow nebulizer (Perkin-Elmer) fitted to a Scott-type, double-pass spray chamber. The plasma operating conditions used are summarized in Table 2.

The microcolumn containing the PSTH–Dowex was a glass tube (3 cm × 3-mm-i.d.) packed to a height of 0.5 cm (GF-AAS method) or 1.0 cm (ICP-AES method) and a weight of 50–200 mg of sorbent, respectively; at both ends of the microcolumn, polyethylene frits were fixed to prevent material loss. The columns were initially flushed with 2 M nitric acid, and the subsequent use of eluents in each operating cycle was sufficient

Table 1. Graphite furnace temperature program ($V_i = 40$ μL)

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow rate (mL min^{-1})
1	110	1	40	250
2	130	4	30	250
3	1600	5	20	250
4	2200	0	5	0
5	2400	1	2	250

Table 2. Optimum operating conditions for ICP-AES determination of platinum

ICP system	
Wavelength	265.95 nm
R.F. generator	
Frequency	40 MHz
Incident power	1.1 kW
Photomultiplier voltage	800 V
Plasma gas flow rate	12 L min^{-1}
Auxiliary gas flow rate	0.6 L min^{-1}
Nebulizer type	Cross-flow
Nebuliser gas flow rate	0.7 mL min^{-1}
Plasma viewing height	15 mm (above the induction coil)

to make the columns ready for reuse for at least 1 year. For GF-AAS method, on the end of this column was placed a piece of sample capillary of the sampler arm to imitate its sample tip (Fig. 1). Thus, the sample tip of the sampler arm was replaced with this microcolumn, permitting normal working of the sampler.

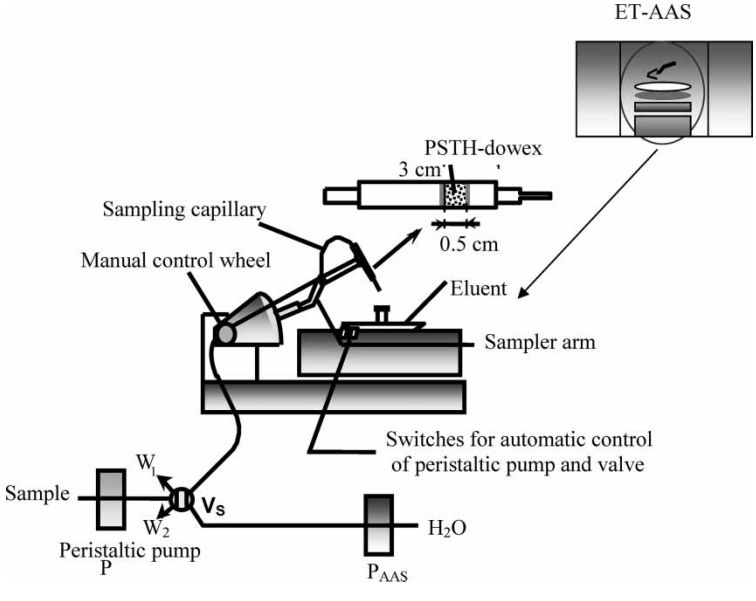

Figure 1. Schematic diagram of FI-GF-AAS system for the preconcentration, separation, and determination of Pt(IV). W_1 and W_2, waste; V_S, selection valve. For further detail, see text.

A peristaltic pump, P (Gilson Minipuls 3), fitted with a vinyl pump tube (Elkay) (1.65-mm-i.d.)., was used for sample loading. A Rheodyne Type 50 six-port rotary valve was used as a switching valve. Transport lines were made from 0.8-mm-i.d. PTFE tubing. The peristaltic pump and the selection valve were readily controlled electronically via two switches on the autosampler that were actuated when the autosampler arm was down. The process was thus fully automated without altering the software of the AA spectrometer.

For ICP-AES method, a schematic diagram of the automated online preconcentration system modified from the Perkin-Elmer FIAS 400 is presented in Fig. 2. Pump P1 was connected to the sampler capillary and the microcolumn through a six-way rotary valve; this valve had the column connected within the sample loop.

For sample digestion, a microwave oven (Microdigest 301) controlled by Prolabo TX-32 was used.

All glassware used was washed with 10% nitric acid for 24 hr and rinsed with de-ionized water immediately before use.

Reagents and Samples

All reagents were of highest available purity and at least of analytical reagent grade. Deionized water (18 MΩ cm^{-1}) obtained from a Milli-Q water system

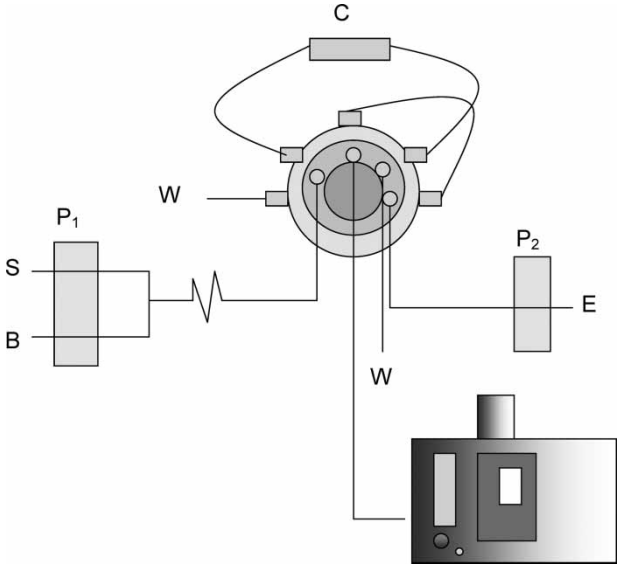

Figure 2. Schematic diagram of FI-ICP system for the preconcentration, separation, and determination of Pt(IV). P_1 and P_2, peristaltic pumps; S, sample; B, buffer; E, eluent; C, sorption column; W, waste.

(Millipore, Bedford, MA, USA) was used throughout. PSTH–Dowex was synthesized as described elsewhere.[20] A standard 1000 μg mL^{-1} Pt(IV) solution (CertiPUR, Merck) was used. Buffer solutions of the required pH were prepared from 0.2 M glycine (Merck) and 0.2 M sodium hydroxide solutions (Merck). HNO_3 (Merck) 2 M was used as eluent.

The certified reference material (CRM) analyzed to determine the accuracy of the proposed procedure was National Institute of Standards and Technology (NIST), Standard Reference Material (SRM) 2557 catalyst. The sample was first prepared in accordance with the instruction of the analysis certificate, after which an accurately weighed amount (0.1 g) was subjected to microwave acid digestion. After digestion, the solution was neutralized with concentrated NaOH and the sample was then diluted to 100 mL with deionized water in a calibrated flask.

River and sea waters were collected in polypropylene bottles previously cleaned by soaking in 0.1 M hydrochloric acid. Samples were filtered by using a membrane of 0.45-μm pore size, acidified to 0.1% (v/v) with concentrated HNO_3, and stored frozen until analysis. The composition of the synthetic sea water was (in g/L): 27.9 of NaCl, 1.4 of KCl, 2.8 of $MgCl_2$, 0.5 of NaBr, and 2.0 of $MgSO_4$, according to the specifications of Weast.[21]

Procedures

GF-AAS Method

The FI manifold is shown in Fig. 1.[22–24] It operated as follows: During the 1-min sample loading period, a 2.4 mL min^{-1} flow of sample (standard or blank) at pH 9.4, buffered with 0.2 M glycine–NaOH, is pumped (via P) through the microcolumn (located in the sampler arm); the metal ion is adsorbed on the sorbent microcolumn and the sample matrix is sent to waste; then, the switching valve (Vs) is actuated and the pumps of the AS-70 furnace autosampler, P_{AAS}, are connected, permitting the operation of the autosampler in the normal mode; a wash step takes place with deionized water and, immediately after, the sampler arm lowers the sample capillary into an autosampler cup (filled with eluent) aspirating 40 μL HNO_3 2 M; then, the sampler arm swings over to the graphite furnace and the tip of the sampler capillary is inserted into the dosing hole of the graphite tube where the eluted Pt(IV) is deposited as a drop; the sampler arm then returns to its initial position and the cycle of the furnace operation commences (Table 1); while the temperature program is running, the switching valve is again turned to start a new loading of the sample (standard or blank); thus, when the spectrometer gives the measurement, the microcolumn is ready for a new injection of eluent. The experimental variables were optimized by conventional univariate method.

ICP-AES Method

The FI manifold used for online preconcentration is shown in Fig. 2. Optimum instrumental conditions are given in Table 2. The FI system was operated as follows: During the 5-min sample loading period, with the valve in FILL position, the sample (standard or blank) was pumped (via pump P_1, at 2.9 mL min^{-1} flow rate), merged with a 0.9 mL min^{-1} flow of buffer in the mixing coil (length 1 cm, i.d. 0.8 mm) and pumped through the microcolumn (located in the sample loop of the valve). The platinum was adsorbed on the mini-column and the sample matrix sent to waste. During the preconcentration step, an 8.4 mL min^{-1} flow of eluent was aspirated from the container by the pump P_2 to establish the baseline of the readout and to stabilize the plasma. At the beginning of the 50-s elution stage, the valve position was changed and the sample pump P_1 was stopped. When the valve was in INJECT position, the eluent flowed through the column. Thus, the accumulated platinum ions were eluted and transferred into the nebulizer of the ICP, and the emission signals were recorded. Then the blank (buffer solution) was pumped through the column for another 30 s to wash off the residual sample matrix. The injector system permitted continuous aspiration of the eluent to the nebulizer to wash and stabilize the plasma. The experimental parameters were optimized by applying a factorial experimental design at two levels and a central composite experimental design. The experimental data was processed making use of the STATGRAPHICS software.[25]

RESULTS AND DISCUSSION

Optimization of Experimental Parameters

To optimize the system, main efforts were focused on the conditions for sample loading and platinum eluting from the column and on the analytical flow system, which was coupled online with the preconcentration and separation unit in order to obtain highly sensitive, accurate, and reproducible results.

Chemical parameters, FI variables, and GF-AAS and ICP-AES parameters were optimized according to the procedure described in "Materials and Methods."

Because the solution pH affects the extent of complexation which in turn determines the percentage of metal retained by the resin, the preconcentration of platinum from solutions buffered at different pH was studied. The range of pH investigated was between 2.0 and 11.0. The results indicate that the optimum pH range was around 8.0–11.0. All subsequent studies were carried out at pH 9.4 and 10.0 using a glycine-NaOH buffer for FI-GF-AAS and FI-ICP-AES, respectively.

The effect of the ionic strength of the medium on the efficiency of the preconcentration was investigated by using different concentrations of buffer. The results obtained for FI-GF-AAS showed that the signal value remains

constant for buffer concentration equal or greater than 0.1 mol L^{-1} up to least 1.0 mol L^{-1}. A 0.2 mol L^{-1} buffer was used for subsequent studies.

It is known that strong acids are effective in dissociating complexes and releasing free metal ions; for these reasons, different acids (HNO_3, HCl, and their mixtures) were tested at different concentrations. The best results were obtained with 2 M HNO_3 solution that was chosen as eluent for this study.

The effect of sample loading time on the absorption or emission signal of Pt was tested at a sample flow rate of 2.4 mL min^{-1}. The signal increased almost linearly with the preconcentration time up to several minutes, after which the slope decreased gradually. Sensitivity enhancements gained by increasing the sample loading time, however, the loading time selected in the experiment was 1 min for GF-AAS method and 5 min for ICP-AES method in order to achieve high sampling frequency with a reasonable degree of sensitivity. Loading time may be higher for samples with low concentrations of platinum. For FI-ICP-AES method, sample flow rate, eluent flow rate, eluent concentration, mixing coil length, and nebulizer flow rate were optimized by a factorial design and subsequently by a central composite design. The optimum conditions obtained are summarized in Table 3.

On the other hand, prior to the analysis of real samples, it was necessary to optimize the instrumental conditions for the determination of platinum by GF-AAS and ICP-AES. The complete program developed as a result of the normal optimization procedure is as described in Table 1 and the optimum operating ICP-AES variables are given in Table 2.

Analytical Characteristics of the Developed Procedures

The characteristic performance data of the FI-GF-AAS and FI-ICP-AES systems for platinum determination are presented in Table 4. The detection

Table 3. Optimal experimental parameters

Technique	GF-AAS	ICP-AES
pH range	8.6–10.4	8.0–11.0
Selected pH	9.4	10.0
Buffer concentration	0.2 M	0.2 M
Eluent	HNO_3 2 M	HNO_3 2 M
Eluent volume	40 μL	—
Eluent flow rate	—	8.4 mL min^{-1}
Sample loading time	Linear up to 5 min for 100 ng mL^{-1}	Linear up to 15 min for 50 ng mL^{-1}
Sample flow rate	2.4 mL min^{-1}	2.9 mL min^{-1}
Buffer flow rate	—	0.9 mL min^{-1}
Nebulizer flow rate	—	0.7 mL min^{-1}
Mixing coil length	—	1 cm

Table 4. Performance of the FI-GF-AAS and FI-ICP-AES systems for platinum determination under the conditions given on the procedure

Analytical parameters	FI-GF-AAS		FI-ICP-AES
	Peak-height	Peak-area	Peak-height
Working concentration range (ng mL^{-1})	0–50	0–100	25–200
Correlation coefficient	0.995	0.998	0.999
Detection limit (ng mL^{-1})	0.5	1.0	7.4
Precision (% RSD, n = 10)	3.0 (C_{Pt} = 10 ng mL^{-1})	1.6 (C_{Pt} = 10 ng mL^{-1})	3.06 (C_{Pt} = 50 ng mL^{-1})
Sampling frequency (hr^{-1})	29	29	10
Enrichment factor	7	14	85
Concentration efficiency (min^{-1})	3.4	7	14.03
Consumptive index (mL)	0.34	0.18	0.17
Preconcentration time (min)	1	1	5

limit was defined as the concentration of analyte giving signals equivalent to three times the standard deviation of the blank plus the net blank intensity. The enrichment factor (EF) was determined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration; the concentration efficiency (CE) was defined as the product of the EF and the sampling frequency in number of samples analyzed per hour; and the consumptive index was calculated as the volume of sample, in milliliters, consumed to achieve a unit EF. These parameters are recommended as criteria for the evaluation of the efficiency and reliability of the design of online column preconcentration for a flow-injection atomic spectrometric system.[26]

Effect of Foreign Ions

The results including significant levels of possible interferents are presented in Table 5. For this study, different amounts of the ionic species tested were added to a solution of platinum. The starting point was an interferent:platinum ratio of 4000 m/m; if any interference occurred, the ratio was gradually lowered until the interference disappeared. The tolerance limits found show that platinum can be determined in the presence of a variety of ions. The ions that interfere most strongly are those that form complexes with PSTH.

Table 5. Tolerance of foreign ions in the determination of platinum

FI-ICP-AES		FI-GF-AAS
	Tolerance ratio	
ion	(m/m)	ion
Br^-, Cl^-, $CO_3^=$, F^-, EDTA, $SO_4^=$, ClO_4^-,	>4000	Mg^{2+}, Pb^{2+}, Ni^{2+}, Ag^+, Hg^{2+}, $SO_4^=$, Br^-, ClO_4^-, Cl^-, $CO_3^=$, F^-, EDTA
	2000	Ca^{2+}, Mn^{2+}, Al^{3+}, Ba^{2+}
Fe^{3+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}	1000	Cr^{3+}
Al^{3+}, Ca^{2+}, Cd^{2+}, Mg^{2+}, Pb^{2+}	500	Cd^{2+}
	250	Cu^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}
Co^{2+}, Cu^{2+}	100	Co^{2+}
Cr^{3+}, Rh^{3+}, Pd^{2+}	10	Rh^{3+}, Pd^{2+}

Sample Analysis

In order to test the accuracy and applicability of the proposed methods for the analysis of real samples, one certified material was analyzed. The result, as the average of the four separate determinations, is shown in Table 6. As can be

Table 6. Results for platinum determination in real samples

		FI-ICP-AES		FI-GF-AAS	
Sample	Certified value (mg kg^{-1})	Found value[a] (mg kg^{-1})	Recovery (%)	Found value[a] (mg kg^{-1})	Recovery (%)
SRM 2557	1131 ± 11	1108 ± 35	97.9	1155 ± 23	102.1
	Added (ng mL^{-1})	Found[a] (ng mL^{-1})	Recovery (%)	Found[a] (ng mL^{-1})	Recovery (%)
River water	5			4.9 ± 0.2	98.0
	10			9.9 ± 0.4	99.0
	25	22.0 ± 4.0	88.0		
Seawater	5			5.1 ± 0.2	102.0
	10			10.4 ± 0.4	104.0
	25	24.0 ± 2.0	96.0		
Synthetic sea-water	5			5.1 ± 0.1	102.0
	10			9.9 ± 0.3	99.0
	25	22 ± 3	88.0		

[a]Means ± SD (n = 4).

seen, the platinum concentration determined by the proposed methods is in close agreement with the certified value.

In view of the application of the methods to the determination of platinum in water, the ability to recover platinum from samples of different water spiked with platinum was investigated. For this purpose, standard solutions containing platinum were added to samples and the resulting material was prepared as described under "Materials and Methods." Standard additions method was used in all instances and the results were obtained by extrapolation. The results of these analyses are summarized in Table 6 and indicated excellent recoveries in all instances.

CONCLUSIONS

Sensitive methods frequently in connection with prior preconcentration are required for the determination of platinum in the environment. There are only a few methods enabling their quantitation at extremely low levels, these are adsorptive stripping voltammetry, nuclear activation analysis, GF-AAS, and ICP-MS. AAS has been used extensively in many laboratories, but detection limits of direct determination, including by GF-AAS, are thus unsatisfactory. On the other hand, optical emission spectroscopy, with argon plasma as the excitation source, has gained worldwide acceptance as a versatile analytical technique. The technique is characterized by low background emission hence superior detection limits, high temperature leading to few chemical interferences, and wide linear response range (5–6 orders of magnitude). Suitable preconcentration techniques prior to the determination by GF-AAS or ICP-AES are solvent extraction, sorption, and ion exchange.

FI online column preconcentration GF-AAS and ICP-AES has revolutionized trace element analysis in samples with complicated matrices.

The experiments performed demonstrate that platinum may be quantitatively adsorbed and preconcentrated on tested sorbent, eluted with nitric acid, and, finally, determined by GF-AAS or ICP-AES. The microcolumn life is very long, at least 1 year, and the only preparation required prior to use is a wash with diluted nitric acid.

The FI-GF-AAS system proposed in this paper has the advantage of being simpler than other FI-GF-AAS systems because the process is fully automated without complicated hardware and software. High speed, ease of use, automation, selectivity, and relative freedom from interference make this method suitable for platinum determination in natural waters samples and Standard Reference Materials.

The FI-ICP-AES system has been shown to be promising for the routine determination of trace amounts of platinum as a result of its simplicity, high efficiency, and good accuracy.

The detection limits were 1.0 ng mL^{-1} (obtained with a 1-min loading time at a sample flow rate of 2.4 mL min^{-1}) and 7.4 ng mL^{-1} (with a 5-min

loading time at a sample flow rate of 2.9 mL min^{-1}) for FI-GF-AAS and FI-ICP-AES, respectively, which compares favorably with others obtained using column solid-phase extraction in FI systems coupled online to conventional atomic spectrometers.[19]

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