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## Knotted Reactors and their Role in Flow- Injection On-line Preconcentration Systems Coupled to Atomic Spectrometry-Based Detectors

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### ABSTRACT

The progress in flow-injection (FI) on-line separation and preconcentration employing knotted reactors (KRs) as a sorption medium for organo-metallic complexes associated to atomic spectrometry techniques is reviewed in this article, focusing the attention on the more frequently complexing agents used. In the last years, the KR has demonstrated to be an excellent alternative in the FI on-line preconcentration procedures; the on-line preconcentration and separation of different metallic species on the inner walls of the KR have been developed utilizing diverse organic and inorganic reagents. The choice of complexing reagents, the coupling of the FI preconcentration system to atomic spectrometry techniques, and the application of the methodologies developed to different samples are discussed.

*Key Words:* Knotted reactors; Preconcentration; Flow-injection; Atomic spectrometry techniques.

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## 1. INTRODUCTION

The combination of flow-injection (FI) coupled to preconcentration and separation methodologies has demonstrated to have a great potential for enhancing the selectivity and sensitivity of atomic spectrometric techniques, such as flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), and inductively coupled plasma-mass spectrometry (ICP-MS). Sample introduction flow rates of the FI systems are usually compatible with the continuous working mode of these techniques and permit on-line operation using relatively simple interfaces.

During the last years, an important number of publications have reported the successful use of knotted reactors (KRs) made from polytetrafluoroethylene (PTFE) tubing for the FI on-line preconcentration and separation of metals, with previous complex formation and subsequent elemental-specific detection by means of different atomic spectrometric techniques. In spite of the relatively low selectivity of the collection medium, usually, sufficient selectivity can be attained by an appropriate complexing reagent and optimization of the experimental conditions.

The retention mechanism in KRs involves changes in the flow direction caused by the knots, creating a secondary flow with some centrifugal force that pushes the particles toward the tubing walls. The KRs made from open tubings produce significantly lower back pressures than packed columns at similar flow-rates, so that higher sample loading rates are readily applicable. The KRs also offer almost unlimited lifetime as well as stability in sorption properties. However, an important limitation of KRs is relatively low retention of sorbed complexes. Typically, retention values in the range of 40–50% are obtained with these preconcentration devices. Nevertheless, this does not lower the overall efficiency of the preconcentration system owing to the much larger flow-rates allowable.

The use of KRs for the on-line sorption preconcentration combined with FAAS determinations was first reported by Fang et al.<sup>[1]</sup> Afterwards, Sperling et al.<sup>[2]</sup> and Yan et al.<sup>[3]</sup> extended the use of such sorption media to applications for on-line preconcentration with ETAAS by adding some improvements to the manifold, such as the addition of a washing step to the preconcentration procedure just after sample loading in the KR, which is aimed at removing residual matrices; and the use of an air flow for both removal of the washing solution and driving the eluate into the graphite tube.

On-line coprecipitation involving collection of precipitates on a PTFE or Microline KR was proposed by Fang et al.<sup>[4]</sup> as an effective preconcentration means for ETAAS. The on-line coprecipitation systems exhibit, generally,

127 higher tolerance to coexisting base metals can be an important benefit in  
128 applications when interferences from such origin are difficult to overcome.  
129 Works developed in Hansen's group<sup>[5-7]</sup> have demonstrated the possibility  
130 of coupling on-line KR coprecipitation to the FI hydride generation (HG)-  
131 atomic absorption spectrometry (AAS) systems employing inorganic copre-  
132 cipitation with carrier reagents and ensuing dissolution in a dilute inorganic  
133 solvent. The elegant aspect of these procedures is that the inorganic precipi-  
134 tates are easily dissolved in diluted acid, which is also the appropriate  
135 medium for the developing HG reaction. The retention of a hydrophilic inor-  
136 ganic coprecipitate requires the KR to be made of a hydrophilic material, such  
137 as cross-linked ethyl vinyl acetate Microline tubing.<sup>[5-7]</sup>

138 In this work, the widespread use of KRs in the on-line preconcentration  
139 systems coupled to atomic spectrometric techniques is revised and discussed  
140 with particular attention to the application of the most common reagents  
141 employed for developing complexing and/or coprecipitating reactions. The  
142 preconcentration and separation procedures by using KRs for real samples  
143 analysis (environmental, biological, and geological ones) are presented in  
144 this article.

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## 148 2. COMPLEXING AND COPRECIPITATING 149 REAGENTS

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151 Due to the relatively low selectivity of the KR, usually, sufficient selec-  
152 tivity can be attained by the use of an appropriate reagent. Additionally, the  
153 low retention capacity of KRs is highly improved by the right selection of a  
154 complexing and/or coprecipitating reagent that interact in a more efficient  
155 manner with the material of which KRs are made.

156 Therefore, hydrophobic reagents are suitable for hydrophobic materials,  
157 whereas hydrophilic reagents are the right choice for hydrophilic materials.  
158 In the literature, several works have reported the use of organic and inorganic  
159 reagents for the preconcentration and separation of metallic and non-metallic  
160 elements on the inner walls of a KR. The selection of an adequate reagent,  
161 principally, depends on its chemical properties and its potential interaction  
162 with the analyte of interest. The most widely used reagents for metal  
163 preconcentration in KR have been so far diethyldithiocarbamate (DDTC),  
164 ammonium pyrrolidine dithiocarbamate (APDC), diethyldithiophosphate  
165 (DDPA), 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP),  
166 8-Hydroxyquinoline (HQ), hexamethylenedithiocarbamate (HMDTC), lantha-  
167 num hydroxide, 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (PMBP), and  
168 dithione, among others.

**KRs and their Role in FI On-line Preconcentration Systems****5**

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**2.1. 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol**

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2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol has been used as a reagent in the spectrophotometric determination of numerous metallic ions,<sup>[8–11]</sup> although precautions had to be taken in order to avoid the precipitation of the corresponding chelate in aqueous media, such as the addition of a surfactant agent. This fact suggests that in the absence of a surfactant 5-Br-PADAP could be a suitable reagent for the preconcentration of various metals on KR.

Several on-line preconcentration systems implemented with KR using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol as complexing reagent of metal ions have been developed in our research group. Among them, vanadium(V) was retained as V(V)–5-Br-PADAP complex on the inner surface of a KR. Decomposition of the organometallic complex and further elution of the analyte were performed by using a diluted solution of nitric acid with subsequent elemental-specific detection by ultrasonic nebulization (USN) coupled to ICP-OES.<sup>[12]</sup> The manifold presented provided a sensitivity enhancement factor of 180 with respect to ICP-OES using pneumatic nebulization (15 for USN and 12 for KR).

In addition, Zn–5-Br-PADAP complex was effectively adsorbed on the inner walls of a KR made of PTFE.<sup>[13]</sup> This system of preconcentration permits the zinc determination in river water samples in concentrations of the order of  $\mu\text{g L}^{-1}$ . The determinations showed good reproducibility and accuracy.

Interestingly, an on-line mercury preconcentration and analysis system by using AAS and FI with cold vapor generation was performed in Ref.<sup>[14]</sup> The results of this work demonstrated the possibility of using 5-Br-PADAP for preconcentration of Hg, since the Hg–5-Br-PADAP complex was effectively adsorbed on the inner surface of a KR. Coupling of the KR to the cold vapor generation system was possible without major modifications relative to conventional systems.

Likewise, Cd has been preconcentrated as Cd–5-Br-PADAP complex in wine and honey samples and the analyte has been determined by USN-ICP-OES and FAAS, respectively.<sup>[15,16]</sup> In the second case mentioned above, the complex adsorbed on a KR was eluted with ethanol as it is known that an organic solvent could significantly improve the sensitivity of FAAS. On the other hand, the use of an organic solvent with ICP-OES detection was not possible, since the high instability generated in the ICP can eventually lead to its extinction.

An on-line Co preconcentration and determination system using a KR implemented in a FI system associated to ICP-OES with USN was also developed in our group.<sup>[17]</sup>

The Co was retained as the complex Co–5-Br-PADAP at pH 8.2. The Co complex was removed from the KR with diluted  $\text{HNO}_3$ . A total enhancement factor of 140 was obtained with respect to ICP-OES using pneumatic

211 nebulization (14.8 for USN and 9.5 for KR). The method was successfully  
 212 applied to the determination of Co in drinking water samples.

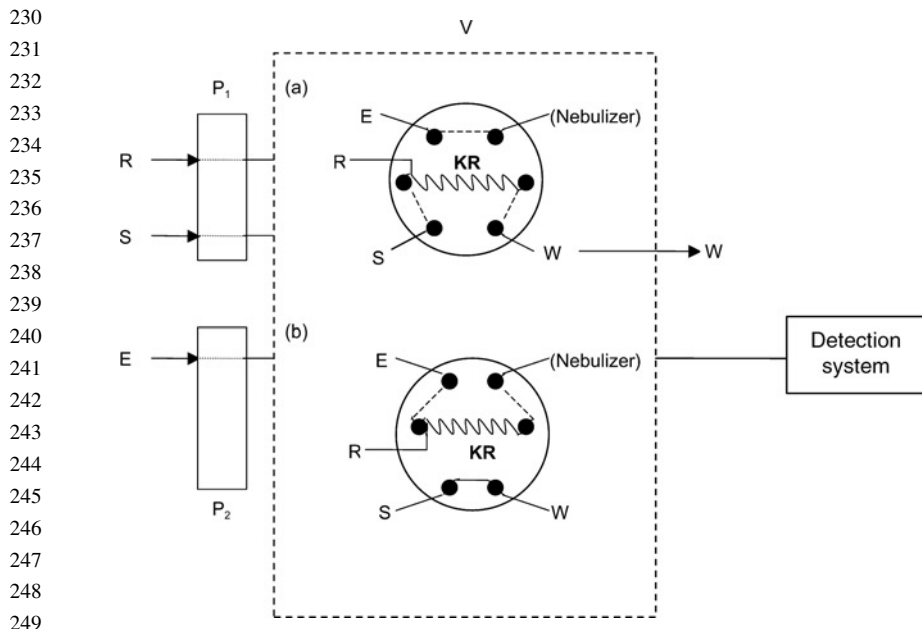
213 Similarly, Sc was retained as the Sc-5-Br-PADAP complex; it was  
 214 removed from the KR with nitric acid, and then it was determined by USN-  
 215 ICP-OES.<sup>[18]</sup> The flexibility of adopting different sample loading times to  
 216 attain different enhancement factors is one of the advantages of the use of  
 217 the mentioned method.

218 Figure 1 shows a general schematic manifold used for metal preconcentration  
 219 on the inner walls of a KR. In Table 1, the most significant figures of  
 220 merit achieved by means of the use of KR in an on-line preconcentration pro-  
 221 cedures and its application to real samples are presented.

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## 2.2. 8-Hydroxyquinoline

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 226 8-Hydroxyquinoline, 2-methyl-8-hydroxyquinoline (CH<sub>3</sub>-HQ), 5,7-  
 227 dichloro-2-methyl-8-hydroxyquinoline (Cl<sub>2</sub>-CH<sub>3</sub>-HQ), 5,7-dibromo-8-hydro-  
 228 xyquinoline (Br<sub>2</sub>-HQ), 5-sulfo-7-iodo-8-hydroxyquinoline (ferron), and  
 229



250 **Figure 1.** Schematic diagram of the instrumental setup. (R): Complexing or coprecipitating  
 251 reagent; (S): sample; (E): eluent; (W): waste; (P<sub>1</sub>, P<sub>2</sub>): peristaltic pumps; (KR):  
 252 knotted reactor; (V): injection valve. Valve positions: (a) sample loading; (b) injection.

## KRs and their Role in FI On-line Preconcentration Systems

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Table 1. The use of KRr in on-line preconcentration procedures and its application to real samples.

Reagent	Analyte	Sample	Eluent	SFR (mL min <sup>-1</sup> )	Precon- centration time	Enrichment factor	Throughput sample (hr <sup>-1</sup> )	LOD (3σ) (μg L <sup>-1</sup> )	Technique	Ref.
5-Br-PADAP	V(V)	Drinking water	Nitric acid	5.0	120	180 <sup>a</sup>	22.0	0.019	USN-ICP-OES	[12]
5-Br-PADAP	Zn	River water	Nitric acid	5.0	120	42	22.0	0.09	ICP-OES	[13]
5-Br-PADAP	Hg	Drinking water	Hydrochloric acid	5.0	300	25	11.0	0.005	CV-AAS	[14]
5-Br-PADAP	Cd	Wine	Nitric acid	5.0	60	216 <sup>a</sup>	40.0	0.005	USN-ICP-OES	[15]
5-Br-PADAP	Cd	Honey	Ethanol	5.0	120	140 <sup>a</sup>	26	0.05	FAAS	[16]
5-Br-PADAP	Co	Drinking water	Nitric acid	5.0	120	140 <sup>a</sup>	22.0	0.03	USN-ICP-OES	[17]
5-Br-PADAP	Sc	River water	Nitric acid	6.0	300	1120 <sup>a</sup>	11	0.00045	USN-ICP-OES	[18]
HQ; CH <sub>3</sub> -HQ; Cl <sub>2</sub> -CH <sub>3</sub> - HQ; Br <sub>2</sub> -HQ; Ferron; SO <sub>3</sub> H-HQ APDC-Fe	Co, Ni, Cd	—	Methanol	—	—	10–34	—	—	ETAAS	[19]
	Co, Ni, Cd	Bovine liver, urine	MIBK	—	—	30 <sup>a</sup> –42 <sup>a</sup>	—	0.3–3.0	FAAS	[20]
APDC	Sb(III)	Water	Ethanol	5.4	30	30 <sup>a</sup>	42	0.021	ETAAS	[3]
APDC	Tl	River sediment	Ethanol	4.8	30	27 <sup>a</sup>	26	0.015	ETAAS	[21]
APDC	Co	Natural waters	Ethanol	—	—	47 <sup>a</sup>	31	0.0028	ETAAS	[22]
APDC	Cr(VI)	Water	Ethanol	5.0	60	19 <sup>a</sup>	21.2	0.0042	ETAAS	[23]
APDC	Cu	Biological samples and sea-water	Methanol	5.0	30	44 <sup>a</sup>	26	0.006	ETAAS	[24]
	Ni		Ethanol	—	30	21 <sup>a</sup>	26	0.0076	ETAAS	[24]

(continued)

Table 1. Continued.

Reagent	Analyte	Sample	Eluent	SFR (mL min <sup>-1</sup> )	Precon- centration time	Enrichment factor	Throughput sample (hr <sup>-1</sup> )	LOD (3σ) (μg L <sup>-1</sup> )	Technique	Ref.
APDC	Cu	Environmental and biological materials	–	–	–	–	–	–	ETAAS	[25]
APDC	Pt	Blood samples	Methanol	8.8	90	112 <sup>a</sup>	21	0.01	ETAAS	[26]
APDC	As	Porewaters	Nitric acid	5.0	60	22 <sup>a</sup>	–	0.021	ICP-MS	[27]
APDC	Cr(VI)	Water	IBMK	5.5	99	18.4	24.2	0.0033	ETAAS	[28]
APDC	Cr(VI)	NIST-Cr(VI) reference material	Ethanol	5.0	60	19	13.8	0.067	ETAAS	[29]
APDC vs. compared with HQ PMBP NNA	Co	Tap water and sea water	Methanol	1.2	120	20.8 <sup>a</sup>	11.1	0.0106	ETAAS	[30]
APDC	Cu, Ni, Sb, Co, Ag, Cd, Mo, In, Pb	Biological and natural water samples	Methanol	2.8	120	5–70 <sup>a</sup>	–	0.0087 0.0081 0.0158 0.0005– 0.026	ICP-TOFMS	[31]
APDC	Fe	Water	Nitric acid	5.0	30	12 <sup>a</sup>	21	0.08	ICP-MS	[32]
APDC	Cr(VI)	Water	Ethanol	5.0	60	16.3	16.7	0.016	ETAAS	[33]
APDC	Cd, Ni, Co, Cu, Pb, Zn, Mo, Cr, W	–	Nitric acid	1.2	120	4–36	–	–	ICP-MS	[34]
Cu-PDC	Hg	Environmental and food CRMs/water	Ethanol	4.5	40	91 <sup>a</sup>	22	0.0062	ETAAS	[35]





Table 1. Continued.

Reagent	Analyte	Sample	Eluent	SFR (mL min <sup>-1</sup> )	Precon- centration time	Enrichment factor	Throughput sample (hr <sup>-1</sup> )	LOD (3σ) (μg L <sup>-1</sup> )	Technique	Ref.
DDTC	Pb	Water	MIBK	-	40	32 <sup>a</sup>	-	2.9	FAAS	[47]
Zn-DDTC	Pb	Human hair, water	MIBK	-	40	-	-	2.7	FAAS	[48]
Cu-DDTC	Cd, Pb, Ni	Environmental samples	IBMK	-	30	22 <sup>a</sup> -45 <sup>a</sup>	65	0.23-3.2	FAAS	[49]
Cu-DDTC	Ag	Geological samples	IBMK	3.6	30	26	72	0.6	FAAS	[50]
Na-DDTC	Pb	Tap water	Hydrochloric acid	10	60	140a	20	0.2	USN-ICP-OES	[51]
DET	Pt, Rd, Pd	Biological fluids and road dust	Methanol	5.0	120	2-55	-	0.00036- 0.00212	ICP-TOFMS	[52]
Dithione	Cu, Cd, Zn, Co	Biological materials	MIBK	5.0	60	23.4-69.3	18	1.06-2.56	FAAS	[53]
La(OH) <sub>3</sub>	Cr	Environmental samples	Hydrochloric acid	6.0	110	22	-	0.8	FAAS	[54]
La(OH) <sub>3</sub>	Cr(III)/ Cr(VI)	Natural water	Hydrochloric acid	6.0	-	22	-	0.8	FAAS	[55]
La(OH) <sub>3</sub>	Se(IV)	Tap and well water	Hydrochloric acid	4.0	100	24	33	0.001	HG-AAS	[5]
La(OH) <sub>3</sub>	Se(IV)	Aqueous standards	Hydrochloric acid	4.8-8.8	99	30-46	33	0.004- 0.006	HG-AAS	[6]
La(OH) <sub>3</sub>	As(III)	Natural water	Hydrochloric acid	4.0	100	32	33	0.003	HG-AAS	[7]
Fe-HMDTC	Cd, Ni	Whole blood digests	IBMK	2.0-3.0	20-40	8-16	-	0.003- 0.02	ETAAS	[4]



463 5-sulfo-8-hydroxyquinoline (SO<sub>3</sub>H-HQ) were compared as chelating reagents  
464 for on-line sorption preconcentration of cobalt in a KR precoated with the  
465 reagent.<sup>[19]</sup> The results obtained with the different HQ derivatives revealed  
466 the properties of the chelating reagent responsible for the processes taking  
467 place in the KR. The influence of hydrophobicity, acidity, stability of the  
468 cobalt chelate, and type of substituents in the HQ ring system on the separate  
469 steps of the FI preconcentration procedure were discussed in this work.  
470 According to the performance characteristics of the different HQ derivatives,  
471 the most important parameters for on-line preconcentration in a KR are the  
472 hydrophobicity of the reagent and the stability of the chelate complex  
473 formed with the analyte. The best performance characteristics obtained for  
474 the CH<sub>3</sub>-HQ system indicate that suitable chelating reagents for on-line  
475 KR precoating preconcentration scheme should be hydrophobic for their sorp-  
476 tion on the hydrophobic walls of KR and should form a stable complex with  
477 the analyte to favor its chemisorption on the KR surface modified by the  
478 immobilized reagent.

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### 481 2.3. Ammonium Pyrrolidine Dithiocarbamate

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483 Ammonium pyrrolidine dithiocarbamate is a well-known group reagent,  
484 suitable for the preconcentration of heavy metal ions from weakly acidic or  
485 neutral solutions. In APDC molecule, there are N and S atoms responsible  
486 for the complexation mechanism.

487 An efficient online co-precipitation system coupled to a FI technique for  
488 cobalt, nickel, and cadmium using Fe-APDC as complexing reagent was  
489 reported by Fang et al.<sup>[20]</sup> The precipitate was dissolved by methyl isobutyl  
490 ketone (MIBK) and directly introduced into the FAAS instrument.

491 In a different study, a FI online sorption preconcentration system has been  
492 synchronously coupled to an ETAAS system for the selective determination of  
493 (ultra)trace amounts of Sb(III) in water.<sup>[3]</sup> The determination was achieved by  
494 selective complexation of Sb<sup>3+</sup> with APDC at a wide range of sample acidity  
495 and sorption of the complex onto the inner walls of a PTFE KR. Quantitative  
496 elution was achieved with 35 μL of ethanol and subsequent ETAAS detection.  
497 In order to minimize dispersion and reduce the eluent volume required for the  
498 elution, an air flow was used to drive the eluent and to deliver all the eluate  
499 into an unpreheated polycrystalline graphite tube without a platform. An intro-  
500 duction of an efficient wash step before elution with the additions of APDC to  
501 the wash medium permitted the use of simple aqueous standards for direct  
502 calibration in the analysis of seawater. The accuracy of the proposed  
503 method was demonstrated by analyzing synthetic mixtures and spiked  
504 seawater.

**KRs and their Role in FI On-line Preconcentration Systems****13**

505           Additionally, Adams et al.<sup>[21]</sup> have developed a method for the determi-  
506           nation of thallium in river sediment by FI on-line sorption preconcentration in  
507           a KR coupled to ETAAS. The  $Tl^{3+}$ -pyrrolidinedithiocarbamate complex  
508           formed in strongly acidic medium was sorbed on the inner walls of a PTFE  
509           KR reactor and quantitatively eluted with 45  $\mu$ L of ethanol. The ETAAS  
510           determination was performed in parallel with the preconcentration of the  
511           next sample. The adsorption efficiency was 51%. The accuracy of the  
512           method was demonstrated by the analysis of a certified reference material.

513           A FI-ETAAS method was developed for the determination of ultra-trace  
514           amounts of cobalt in natural waters.<sup>[22]</sup> The preconcentration was achieved  
515           by online complexation of cobalt with APDC and subsequent sorption of  
516           the complex onto the inner walls of a KR. In this work, in order to reduce  
517           the eluate volume and to minimize dispersion, an air flow was used to  
518           drive the eluent for the elution of the adsorbed analyte and dispel the eluate  
519           into the graphite tube.

520           Nielsen and Hansen<sup>[23]</sup> have reported a work which describes the precon-  
521           centration and determination of ultra-trace amounts of Cr(VI) via on-line reac-  
522           tion with APDC and formation of the Cr(VI)-PDC complex. The  
523           preconcentration was performed by adsorption on the inner wall of a KR.  
524           The complex was eluted with a monosegmented discrete zone of ethanol,  
525           and the analyte was quantified by ETAAS. The operation of the FI-system  
526           and the ETAAS detector were synchronously coupled.

527           A FI system with on-line sorption preconcentration of copper, nickel, and  
528           manganese with APDC or 8-hydroxyquinoline in a PTFE KR using FI tech-  
529           niques was developed.<sup>[24]</sup> APDC offered better performance characteristics  
530           than HQ for the preconcentration of copper and nickel but could not be  
531           employed for manganese. This may be related to the higher stability of their  
532           pyrrolidinedithiocarbamate complexes in comparison with the quinolate  
533           complexes, resulting in higher adsorption efficiency and permitting efficient  
534           washing of the system, and the higher selectivity of complexation in acidic  
535           medium where pyrrolidinedithio-carbamates are formed in comparison with  
536           the pH region quinolate formation. For manganese, HQ gave a better per-  
537           formance than APDC, which could be explained by its stronger affinity to  
538           oxygen-containing than to sulfur-containing reagents. The application of the  
539           KR sorption preconcentration system using HQ for the determination of  
540           copper, nickel, and manganese in biological samples reveals that satisfactory  
541           analytical results can be obtained even with an adsorption efficiency of about  
542           15%.

543           KRs have also been employed in fully automated preconcentration  
544           systems. Velasco-Arjona and co-workers<sup>[25]</sup> have described an automated  
545           robotic method for sample pretreatment developed for copper determination  
546           in environmental and in biological materials at the low mg/kg level.

547 The robotic station performing the preliminary operations as weighing of  
548 sample and acid digestion was coupled with the FI on-line sorption preconcentration  
549 of the pyrrolidine dithiocarbamate chelate of copper on the walls of a  
550 PTFE KR and subsequent ETAAS determination of copper. The accuracy of  
551 the method was demonstrated by the analysis of environmental and biological  
552 certified reference materials.

553 A FI on-line sorption preconcentration method for the electrothermal  
554 AAS determination of platinum was developed.<sup>[26]</sup> The pyrrolidine dithiocarbamate  
555 complexes of either  $\text{Pt}^{4+}$  or  $\text{Pt}^{2+}$ , formed in  $0.7 \text{ mol L}^{-1} \text{ HNO}_3$ , is  
556 adsorbed on-line on the inner walls of a PTFE KR and subsequently eluted  
557 with methanol. The high sensitivity of the method permitted to monitor the  
558 platinum level in the blood of patients treated with platinum-containing  
559 drugs using very small sample volumes, which makes it particularly suitable  
560 for clinical analysis when only small samples can be obtained.

561 It has to be pointed out that the employment of KRs for separation and  
562 preconcentration of elemental species developed by non-chromatographic  
563 methodologies. An interesting method has been developed for determination  
564 of (ultra)trace amounts of As(III) and As(V) in water by FI on-line sorption  
565 preconcentration and separation coupled with ICP-MS by using a KR.<sup>[27]</sup>  
566 The determination of As(III) was achieved by selective formation of the  
567 As(III)–pyrrolidine dithiocarbamate complex, its adsorption onto the inner  
568 walls of the PTFE-KR, elution with a nitric acid solution, and detection  
569 by ICP-MS. Total inorganic arsenic was determined after prereduction of  
570 As(V) to As(III) in a 1% (m/v) L-cysteine– $0.03 \text{ mol L}^{-1} \text{ HNO}_3$  media.  
571 The concentration of As(V) was calculated by difference between the total  
572 inorganic arsenic and As(III). The method was applied to the speciation  
573 analysis of inorganic arsenic in porewaters. It should be noted that no conversion  
574 in the oxidation states of the two arsenic species is mentioned in  
575 this work.

576 A rapid, robust, sensitive, and selective time-based FI on-line solvent  
577 extraction system interfaced with ETAAS is described for analyzing ultra-  
578 trace amounts of Cr(VI) by Hansen et al.<sup>[28]</sup> The sample was initially mixed  
579 on-line with isobutyl methyl ketone (IBMK). The Cr(VI) was complexed by  
580 reaction with APDC, and the non-charged Cr(VI)–PDC chelate formed was  
581 extracted into IBMK in a KR made from PTFE tubing. The organic extractant  
582 was separated from the aqueous phase by a gravity phase separator with a  
583 small conical cavity and delivered into a collector tube, from which  $55 \mu\text{L}$   
584 of the organic concentrated were subsequently introduced via an air flow  
585 into the graphite tube of the ETAAS instrument. The operation of the FI-  
586 system and the ETAAS detector are synchronously coupled. The proposed  
587 method was successfully evaluated by analyzing a NIST Cr(VI)-reference  
588 material, synthetic seawater, and waste waters, and waste water samples from

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589 an incineration plant and a desulfurization plant, respectively. Afterwards,  
590 Nielsen and Hansen<sup>[29]</sup> have described a two time-based FI preconcentration  
591 procedures for the analysis of ultra-trace level concentrations Cr(VI). While  
592 the first approach exploits preconcentration by an on-line formation and  
593 extraction into MIBK of the non-polar complex formed of Cr(VI) ions with  
594 APDC, the second one is based on the formation of the same complex com-  
595 pound and adsorption of it in an incorporated KR which is subsequently  
596 eluted by a discrete volume of ethanol. In both cases, the detection of the  
597 analyte in the eluent is executed by ETAAS. Using a syringe pump based  
598 FI-system, FIAIab-3500, the communication discusses and emphasizes the  
599 performance of these on-line preconcentration/separation procedures. The  
600 developed systems were applied for the assay of Cr(VI) in a NIST reference  
601 material with good recoveries in both instances.

602 Benkhedda and co-workers<sup>[30]</sup> have developed a very sensitive and selec-  
603 tive procedure for the determination of cobalt in natural waters by on-line FI  
604 sorption preconcentration of metal chelate complexes on the walls of a PTFE  
605 KR coupled to ETAAS determination. Several complexing reagents were  
606 compared for this system [APDC, 8-hydroxyquinoline, 1-phenyl-3-methyl-  
607 4-benzoylpyrazol-5-one, and 2-nitroso-1-naphthol-4-sulfonic acid (NNA)].  
608 PMBP offered the best performance characteristics for the preconcentration  
609 of Co and methanol was used as eluent. The efficient sorption of PMBP on  
610 the KR (49.6%) may be attributed to the large conjugated system involving  
611 three rings, phenyl, benzoyl, and pyrazole. The ring systems of HQ, NNA,  
612 and APDC (quinoline, naphthalene, and pyrrolidine, respectively) are  
613 smaller in comparison with those of PMBP and are correspondingly less effi-  
614 ciently sorbed. The interference caused by Al(III) was overcome by the use of  
615 fluoride as a masking agent, whereas the interferences from Cu, Fe(II), and  
616 Fe(III) were masked by thiourea. Also, Benkhedda and co-workers<sup>[31]</sup> have  
617 described a method for on-line sorption preconcentration in KR of traces of  
618 Cu, Ni, Sb, Co, Ag, Cd, Mo, In, and Pb in biological materials and natural  
619 water samples and their determination by axial inductively coupled plasma  
620 time-of-flight mass spectrometry (ICP-TOFMS) with USN. The ability to  
621 collect complete mass spectra at a high frequency (more than 20,000 complete  
622 mass spectra per second) makes ICP-TOFMS nearly ideal for the detection of  
623 FI (transient) signals. The analytes were complexed with APDC from acidic  
624 solutions in the flow system and sorbed onto the KR. The relatively small  
625 volume of methanol used as eluent, along with the employment of an ultra-  
626 sonic nebulizer with membrane desolvation, minimizes the problems pro-  
627 duced by the introduction of organic solvents into the plasma.

628 A method has been developed for the speciation of Fe(III) and Fe(II) by  
629 on-line coupling of FI separation and preconcentration with ICP-MS.<sup>[32]</sup>  
630 Selective determination of Fe(III) in the presence of Fe(II) was made possible

631 by on-line formation and sorption of the Fe(III)–PDC complex in a PTFE KR.  
632 The concentration of Fe(II) was obtained as the difference between Fe(III +  
633 II) and Fe(III) concentrations. A retention efficiency of 80% was obtained.  
634 The method was successfully applied to the determination of trace dissolved  
635 Fe(III) and Fe(II) in local tap water, river water, and groundwater samples.

636 A comparison of using an open tubular PTFE KR and a column reactor  
637 packed with PTFE beads was developed by Hansen et al.<sup>[33]</sup> A FI on-line sorp-  
638 tion preconcentration procedure utilizing a packed column reactor and combin-  
639 ed with ETAAS is proposed for the determination of low levels of  
640 Cr(VI) in water samples. PTFE beads packed in a mini-column is used as  
641 sorbent material. The complex formed between Cr(VI) and APDC is sorbed  
642 on the PTFE beads, and is subsequently eluted by an air-monosegmented dis-  
643 crete zone of absolute ethanol (35  $\mu$ L), the analyte being quantified by  
644 ETAAS. The preconcentration procedure using the proposed column signifi-  
645 cantly enhances the preconcentration efficiency as compared with the precon-  
646 centration approach incorporating an open tubular PTFE KR. Comparing the  
647 two procedures for equal surface sorption area, the advantages of using a  
648 packed column are observed in terms of limit of detection, enrichment  
649 factor (EF), and retention efficiency.

650 Similarly, a comparison of the preconcentration efficiency expressed as  
651 EF in KR and serpentine reactors (SR) for FI sorption and preconcentration  
652 for the off-line determination of Cd(II), Ni(II), Co(II), Cu(II), Pb(II), Zn(II),  
653 Mo(VI), Cr(VI), and W(VI) with ICP-MS was investigated by Liawruangrath  
654 and co-workers.<sup>[34]</sup> The preconcentration was carried out by the formation of  
655 metal–pyrrolidine dithiocarbamate complex in an acidic solution and  
656 sorbed onto the inner wall of the PTFE reactors. The EFs were determined  
657 as the ratio between the analyte intensities after preconcentration using the  
658 reactors and that obtained without using the reactors. Comparing the two  
659 procedures for the equal reactor length (150 cm), the higher EFs obtained  
660 by using KR were observed for all elements. The results obtained indicate  
661 that the KR is preferable to use for the FI sorption preconcentration system  
662 over the SR.

663 Jiang and Yan<sup>[35]</sup> have developed a novel methodology for the determi-  
664 nation of trace mercury in environmental and foods samples by online coupl-  
665 ing of FI displacement sorption preconcentration in a KR to ETAAS.  
666 The developed methodology involved the online formation of copper pyrroli-  
667 dine dithiocarbamate (CuPDC), presorption of the resulting Cu-PDC onto the  
668 inner walls of the KR, and selective retention of the analyte Hg(II) onto the  
669 inner walls of the KR through online displacement reaction between Hg(II)  
670 and the presorbed Cu-PDC. The retained analyte was subsequently eluted  
671 with ethanol and online detected by ETAAS. No additional chemical modi-  
672 fiers for the stabilization of mercury were required in the present system



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673 owing to the stability of Hg-PDC at the drying stage, and no pyrolysis stage  
674 was necessary due to the effective removal of the matrices.

675 A novel on-line FI multiplexed sorption preconcentration procedure with  
676 repetitive sample injections was developed.<sup>[36]</sup> In contrast to previous FI pre-  
677 concentration systems, the proposed multiplexed preconcentration procedure  
678 evenly divides a single longer sample injection step into several shorter sub-  
679 steps while the total preconcentration time is still kept constant. To demon-  
680 strate its merits, the proposed FI on-line KR multiplexed sorption  
681 preconcentration system was combined with FAAS for determination of  
682 trace lead in water, tea, and herb medicines. The lead in the sample solution  
683 on-line reacted with APDC, and the resultant analyte complex was sorbed  
684 on the inner walls of the KR. The residual sample solution was then  
685 removed from the KR with an air flow. The above two steps were repeated  
686 eight times with a total preconcentration time of 120 sec. The sorbed  
687 analyte was eluted from the KR with diluted HCl for on-line FAAS detection.  
688 The present multiplexed preconcentration procedure with eight repetitive  
689 sample injections for a total preconcentration time of 120 sec gave a retention  
690 efficiency of 92%, twice than that obtained by one single sample injection  
691 preconcentration (47%).

692 Yan and co-workers<sup>[37]</sup> have reported a FI on-line sorption preconcentra-  
693 tion and separation in KR coupled to hydride generation atomic fluorescence  
694 spectrometry (HG-AFS) for speciation of inorganic arsenic in natural water  
695 samples. The method involved on-line formation of the As(III)–pyrrolidine-  
696 dithiocarbamate complex, its adsorption onto the inner walls of the KR,  
697 elution with HCl, and detection by HG-AFS. Total inorganic arsenic was  
698 determined after prereduction of As(V) to As(III) with 1% m/v L-cysteine.  
699 The concentration of As(V) was calculated by the difference of the total inor-  
700 ganic arsenic and As(III). Potential factors that affect adsorption, rinsing,  
701 elution, and hydride generation were investigated in detail. The low cost,  
702 easy operation, and high sensitivity are the obvious advantages of the  
703 present system. The developed method was also successfully applied to the  
704 speciation of inorganic arsenic in local natural water samples.

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**2.4. Diethyldithiophosphate**

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709 Yan and Adams<sup>[38]</sup> describe, in their paper, a robust and selective FI on-  
710 line separation and preconcentration procedure for the ETAAS determination  
711 of lead in biological and environmental samples. DDPA was chosen as the  
712 complexing agent since it is more selective for lead in the presence of other  
713 heavy metals than the dithiocarbamates. With the use of diethyldithio-  
714 phosphite as complexing agent and citric acid as masking agent, the analyte

715 complex was selectively formed and sorbed on the inner walls of a PTFE KR.  
716 The complex Pb–DDP was eluted from the KR with a discrete volume of  
717 ethanol and the eluate was directly introduced into the graphite tube by an  
718 air flow. DDPA was chosen as the complexing agent since it is more selective  
719 for lead in the presence of other heavy metals than the dithiocarbamates. In  
720 this work, the adsorbed Pb–DDP complex was found to be easily removed  
721 with diluted nitric acid or even deionized water, probably due to the instability  
722 of the Pb–DDP complex. During the KR rinsing, the authors have reported the  
723 necessity to add appropriate amounts of DDPA and citric acid to the rinsing  
724 solution in order to prevent analyte loss. Also, DDPA has been used for the  
725 preconcentration of bismuth on the inner walls of a KR by Ivanova and co-  
726 workers.<sup>[39]</sup> DDPA was chosen as chelating reagent in this work due to its  
727 stability in the acidic medium in which the bismuth complex is formed. The  
728 complex Bi–DDP was quantitatively eluted from the KR with hydrochloric  
729 acid and the eluate was directly introduced into a pyrolytically graphite  
730 tube. The results obtained demonstrate the feasibility of using an on-line  
731 KR sorption preconcentration ETAAS system for the determination of  
732 bismuth in sediment and cod muscle samples.

733 In addition, Ivanova and co-workers<sup>[40]</sup> have employed diethyldithiophos-  
734 phate as complexing agent for the preconcentration of cadmium and lead and  
735 their determination in blood by ETAAS. The analyte complexes were selec-  
736 tively adsorbed on the KR and eluted from the 100 cm KR with methanol.  
737 DDPA was chosen as the chelating reagent in this work due to stability in  
738 acidic medium and high selectivity for lead and cadmium in the presence of  
739 alkali, alkaline earth, and heavy metal ions. Compared with FI-ETAAS, the  
740 present system offers higher enhancement factors and lower detection limits.  
741 A further advantage over the latter method is the on-line purification of the che-  
742 lating reagent, which allows the use of a concentrated reagent and washing sol-  
743 ution without any appreciable blank. The performance of the method permitted  
744 its successful application to the monitoring of (ultra) trace cadmium and lead  
745 concentrations in blood.

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## 2.5. Diethyldithiocarbamate

751 A new on-line preconcentration FAAS system for trace cadmium deter-  
752 mination was developed based on sorption of soluble metals complexes on  
753 the walls of a PTFE KR using FI techniques.<sup>[11]</sup> Cadmium complexed with  
754 sodium DDTC was sorbed on the inner walls of the reactor and eluted on-  
755 line by IBMK. The retention efficiency was 81% at a sampling loading rate  
756 of  $5.2 \text{ mL min}^{-1}$ . Thiourea and ascorbic acid/phenanthroline were used to

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757 overcome interferences from copper and iron, respectively. The system was  
758 applied to the determination of cadmium in biological materials.

759 Fang et al.<sup>[41]</sup> have proposed a FAAS determination of silver in geological  
760 materials using a FI system with on-line preconcentration by coprecipitation  
761 with DDTC. The analyte was preconcentrated and separated from the bulk  
762 of the matrix by on-line coprecipitation with the Fe(II)–DDTC complex in  
763 the presence of 1,10-phenanthroline in a FI system. The precipitate was col-  
764 lected in a KR without using filter. The precipitate was dissolved in IBMK  
765 and introduced directly into the nebulizer–burner system of an AAS. 1,10-  
766 Phenanthroline was added to the sample solution to mask large concentrations  
767 of iron(II).

768 Moreover, a FI online adsorption preconcentration FAAS system for the  
769 determination of Cu was developed by Fang et al.<sup>[42]</sup> The Cu-DDTC chelate  
770 was adsorbed on the walls of a PTFE KR. The sorbed species was eluted by  
771 IBMK and air segmentation between sample and eluent was employed to  
772 avoid mixing of the neighboring phases under fast elution rates. The  
773 method was applied successfully to the determination  $\mu\text{g L}^{-1}$  amounts of  
774 Cu in drinking water and sea water and  $\mu\text{g g}^{-1}$  amounts of Cu in rice.

775 In addition, a FI on-line sorption preconcentration electrothermal atomic  
776 absorption spectrometric system for fully automatic determination of lead in  
777 water was investigated by Welz et al.<sup>[2]</sup> This FI manifold has been developed  
778 with the aim of reducing the eluate volume and minimizing dispersion. The  
779 Pb-DDTC complex was adsorbed on the inner walls of a KR made of PTFE  
780 tubing. After that, an air flow was introduced to remove the residual solution  
781 from the KR and the eluate delivery tube, and then the adsorbed analyte  
782 chelate was quantitatively eluted into a delivery tube with 50  $\mu\text{L}$  of ethanol.  
783 An air flow as used to propel the eluent from the eluent loop through the  
784 reactor and to introduce all the ethanolic eluate onto the platform of the trans-  
785 versely heated graphite tube atomizer, which was preheated to 80°C. The  
786 adsorption efficiency was 58%, and the enhancement factor was 142.

787 On the other hand, a preliminary implementation of FI on-line precipi-  
788 tation with ICP-MS was applied to the determination of Cu in certified  
789 estuarine water by Beauchemin et al.<sup>[43]</sup> A solution of sodium DDTC  
790 (NaDDTC) in ammonium acetate was used as precipitant, which was mixed  
791 online with samples. The precipitate was collected in a KR/filter system,  
792 and subsequently dissolved using nitric acid for the delivery to ICP-MS.  
793 The KR/filter system was heated to enhance the precipitation and dissolution  
794 processes.

795 Similarly, Beauchemin et al.<sup>[44]</sup> have described a FI on-line precipitation  
796 system coupled to ICP-MS and it was applied to the determination of Cr, Mn,  
797 Fe, Co, Ni, and Cu in certified estuarine water. NaDDTC was used as  
798 group-selective precipitant. Analyte preconcentration and separation from

799 the matrix in NaDDTC is indeed more selective than the precipitation of  
800 hydroxides for the analysis of sea-water since it does not react with Na, Ca,  
801 or Mg. A solution of NaDDTC in ammonium acetate (at pH 6.75) was  
802 mixed with samples on-line to ICP-MS. The precipitates were collected in a  
803 KR-filter system, washed with deionized distilled water, and then dissolved  
804 in diluted nitric acid (containing  $10 \mu\text{g L}^{-1}$  Ga as an instrumental drift  
805 monitor) for delivery to ICP-MS. The KR/filter system was heated (at  
806 around  $70^\circ\text{C}$ ) to enhance the precipitation and dissolution processes. An external  
807 calibration using aqueous standards in 1%  $\text{HNO}_3$  provided results in good  
808 agreement with the certified values (with a correction for drift). The proposed  
809 approach features two novelties for ICP-MS: the use of an organic precipitant  
810 without any coprecipitation carrier; and heating the KR-filter system to  
811 enhance the precipitation and dissolution processes.

812 Jiang et al.<sup>[45]</sup> have described a novel FI on-line displacement/sorption  
813 preconcentration and separation techniques coupled with FAAS for the deter-  
814 mination of trace copper in complicated matrices. The methodology involved  
815 on-line formation of lead diethyldithiocarbamate (Pb-DDTC), presorption of  
816 the resultant Pb-DDTC onto the inner walls of the KR, retention of the  
817 analyte Cu(II) on the inner walls of the KR through a displacement reaction  
818 between Cu(II) and the sorbed Pb-DDTC (because the stability of Cu-  
819 DDTC is greater than Pb-DDTC) and elution of the retained analyte with  
820 ethanol for FAAS detection. Interference from co-existing ions with lower  
821 stability DDTC complexes relative to Pb-DDTC were eliminated without  
822 need for any masking reagents in the proposed system. The developed  
823 system was successfully applied to interference free determination of trace  
824 copper in a variety of environmental and biological materials with high con-  
825 tents of co-existing heavy metals.

826 On the other hand, Liu and co-workers<sup>[46]</sup> developed an on-line coprecipi-  
827 tation system with DDTC-Ni(II) coupled to FAAS for the determination of  
828 trace Cu, Pb, Cd, and Fe in environmental and biological samples. Metal  
829 ions were on-line co-precipitated with DDTC-Ni(II) in diluted  $\text{HNO}_3$ , the  
830 precipitate was collected in a KR, and it was then dissolved in IBMK. The  
831 concentrated zone was transported directly into the nebulizer-burner  
832 system of a FAAS. Enhancement factors of 60, 58, 65, and 59 were obtained  
833 for Cu, Pb, Cd, and Fe, respectively. The developed method was applied to  
834 determination of the metals in waters and environmental reference material  
835 of soil, and biological reference materials of mussel and human hair. Satisfac-  
836 tory results were obtained.

837 A FI on-line adsorptive preconcentration system with a KR for FAAS  
838 determination of trace Pb in water was developed by Jin and co-workers.<sup>[47]</sup>  
839 The lead chelate of DDTC formed online was concentrated by adsorption  
840 on the inner wall of a KR made of PTFE tubing. The sorbed lead species

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841 was eluted with MIBK and directly transported to the nebulizer of FAAS. The  
842 manifold allowed for a system of one peristaltic pump and one injection valve  
843 to perform automatic preconcentration–elution. Interferences from common  
844 diverse ions such as  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  were removed by addition of 0.5%  
845 ascorbic acid, 0.1% *o*-phenanthroline and 1% thiourea into the test solution.  
846 The developed method has been applied to the determination of trace lead  
847 in various water samples.

848 Moreover, a FI on-line coprecipitation system operating at high acidity  
849 and coupled with FAAS for trace lead determination was proposed by Jin  
850 and Chen.<sup>[48]</sup>  $\text{Pb}^{2+}$  was coprecipitated with Zn–DDTC in  $0.5 \text{ mol L}^{-1}$  HCl.  
851 The precipitates were collected in a KR, and then eluted and transferred  
852 into the AAS nebulizer with MIBK. The method was successfully used for  
853 the determination of trace Pb in human hair and water samples.

854 A novel on-line coprecipitation–preconcentration system with DDTC–  
855 Cu(II) being used as a carrier for the flame atomic absorption spectrometric  
856 determination of trace cadmium, lead, and nickel was developed.<sup>[49]</sup> Sample  
857 solutions, spiked with  $\text{Cu}^{2+}$  and acidified with hydrochloric acid, were  
858 merged on-line with DDTC solution in a “T” connector upstream of a KR.  
859 The analytes were coprecipitated with DDTC–Cu(II) and collected on the  
860 inner wall of the KR. The collected species were eluted with IBMK, and  
861 the effluent was transported directly into the nebulizer. The method has  
862 been successfully applied to the determination of trace cadmium, lead, and  
863 nickel in various water samples and a standard reference soil.

864 Afterward, Mao and co-workers<sup>[50]</sup> developed an on-line coprecipi-  
865 tation–preconcentration system with DDTC chelate of copper as the copre-  
866 cipitate carrier coupled to FAAS for the determination of trace silver. Ag  
867 was on-line coprecipitated with DDTC–Cu(II) and the precipitate was col-  
868 lected in a KR. The precipitate was then dissolved by IBMK and transported  
869 directly into the nebulizer–burner system of a FAAS. The developed method  
870 has been successfully applied to the determination of trace amount of silver in  
871 geological samples.

872 An on-line Pb preconcentration and the determination system  
873 implemented with ICP-OES combined with a FI method with USN was  
874 studied by Salonia et al.<sup>[51]</sup> The lead was retained as the Pb–DDTC  
875 complex at pH 9.5. The lead complex was eluted from the KR with diluted  
876 hydrochloric acid. A total enhancement factor of 140 was obtained with  
877 respect to ICP-OES using pneumatic nebulization (14.8 for USN and 9.5 for  
878 KR). The manifold presented provided a 65% recovery of the Pb–DDTC  
879 complex from the KR. The preconcentration system together with USN per-  
880 mitted lead determination in tap water samples in which its concentration  
881 was in the  $\mu\text{g L}^{-1}$  range. The determination showed good reproducibility  
882 and accuracy.

## 2.6. Diethylthiourea

*N,N*-dialkyl-*N'*-benzoylthioureas have been found particularly successful for the selective preconcentration of Platinum Group Metals even from strongly interfering matrices. Owing to the low solubility of these reagents in water, they have been used as aqueous-alcoholic solutions.

An ICP-TOF-MS with ultrasonic nebulization combined on-line with a FI system for the determination of Pt, Rh, and Pd in biological fluids and road dust was reported by Adams et al.<sup>[52]</sup> Simultaneous and selective preconcentration of the three analytes was performed by sorption of their complexes formed on-line with diethylthiourea (DET) on the inner walls of a PTFE KR. A quantitative elution was achieved using methanol acidified with HNO<sub>3</sub>. Special attention was paid to the study of the adverse effects of potentially interfering species present in the matrix. Under optimum conditions of preconcentration, nebulization, and detection, detection limits in the sub ng L<sup>-1</sup> range, 0.54, 0.36, and 2.12 ng L<sup>-1</sup> for Pt, Pd, and Rh, respectively were obtained. The main advantages of this approach are the complete separation from the matrix and especially for Pd and Pt the enrichment achieved, enabling interference free determination at low ng L<sup>-1</sup> levels.

## 2.7. Dithione

In dithione molecule there are four N atoms and one S atom. The reaction between heavy metal ions and this chelator is the total results of ammoniation and sulfuration. Many heavy metal ions, which are inclined to form specific sulfides, will be able to be extracted by dithione. These ions often have “d” electron orbit unfilled (such as Cu, Co, Cd, Ni, Pt, etc.) or have 10 “d” electrons (such as Zn, Pd, Bi, Hg, In, etc.). Besides, the increase of coordinating atoms in chelators leads to the increase of chelating ability with metal ions.

A procedure using dithione as chelator in a FI-KR-FAAS system to determine trace amounts of Cu, Cd, Zn, Co in biological standard samples has been described by Shuyu and co-workers.<sup>[53]</sup> Regarding the possibility of interferences elimination, alkali, and alkaline earth elements, which could not chelate with dithione, were separated from the objective metals and the competition between trace metals was avoided due to the strong chelating ability of dithione. In this work, three chelating reagents (APDC, NaDDTC, and dithione) were also compared. Dithione showed the better results due to its capacity to overcome interferences and reach higher concentration factors.

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## 2.8. Lanthanum Hydroxide

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## 2.9. Hexamethylenedithiocarbamate

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A FI on-line coprecipitation system has been coupled to ETAAS for the determination of trace amounts of cadmium and nickel in whole blood digests by Fang and Dong.<sup>[4]</sup> Cd and Ni were coprecipitated with the

967 Fe(II)–hexamethylenedithiocarbamate complex on the walls of a KR without  
968 using a filter. The precipitate was dissolved in IBMK and stored in a PTFE  
969 tube before introduction onto the platform of a graphite furnace carried by a  
970 stream of HMDTC reagent. EFs of 16 and 8 were obtained for cadmium  
971 and nickel, respectively, using 20 and 40 sec precipitation collection times.  
972 Recoveries of cadmium and nickel in blood digests were 103% and 106%,  
973 respectively.

974 In an early work developed by Welz et al.,<sup>[56]</sup> a procedure for the copre-  
975 cipitation of lead in the presence of high concentrations of iron, originally  
976 described as a batch process, was modified and adapted to on-line preconcentration using a FI system FAAS. Lead was coprecipitated quantitatively with the Fe(II)–HMDTC complex and collected in a KR made of Microline tubing without using a filter. The precipitate was dissolved in IBMK and introduced directly into the nebulizer–burner system of FAAS. An EF of 20 and an enhancement factor of 66 were obtained for a coprecipitation time of 30 sec. The results obtained for the determination of lead in reference materials (blood and bovine liver) demonstrated the applicability of the procedure to the analysis of biological materials.

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#### 987 2.10. Ion-Pairing Reagents

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989 By FI on-line preconcentration of the ion-pair of the negatively charged  
990 cobalt-nitroso-R-salt complex with the tetrabutylammonium cation on the  
991 KR, an accurate and precise method for the ETAAS determination of cobalt  
992 in biological samples and natural waters was developed.<sup>[57]</sup> The FI on-line  
993 sorption preconcentration of ion-pairs on the inner walls of the KR was  
994 shown to be an effective approach for trace element preconcentration in  
995 ETAAS. It provides possibilities for analyte preconcentration as a charged  
996 complex compensated by a suitable counter-ion. The effect of potential inter-  
997 ferents encountered in biological samples and natural waters on the precon-  
998 centration and determination of cobalt was studied under the optimum  
999 chemical and FI conditions. The results showed a good tolerance to inter-  
1000 ferences. A better tolerance was achieved by the addition of a suitable  
1001 masking agent.

1002 On the other hand, a rapid, sensitive, accurate, and precise FAAS method  
1003 is described for the determination of cadmium in mussels by Yebra and  
1004 co-workers.<sup>[58]</sup> The method is based on the continuous precipitation of  
1005 cadmium as an ion-pair between tetraiodocadmate and quinine (tetraiodocad-  
1006 mate reacts with several alkaloids by their protonated tertiary nitrogens to  
1007 form white or yellow ion-pairs insoluble in water and soluble in alcohol),  
1008 the precipitate was retained on a filter device, and then it was dissolved



1009 with ethanol. The method demonstrates high tolerance to interferences, and  
1010 the data obtained are in agreement with the certified value of a selected refer-  
1011 ence material. This procedure was applied to the determination of cadmium in  
1012 mussel samples from estuaries in Galicia (Spain).  
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### 1015 2.11. Sodium Hydroxide

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1017 A simple strategy for preconcentration of metal species in KRs consists in  
1018 the precipitation of metal ions as their insoluble hydroxides. This can be easily  
1019 achieved in the presence of a strong base such as sodium hydroxide. A  
1020 general rapid on-line preconcentration method for the determination of trace  
1021 metals coupled to FAAS or ion chromatography (IC) with spectrophotometric  
1022 detection is described by Cámara et al.<sup>[59]</sup> The method was based on the on-  
1023 line precipitation of metal hydroxides with sodium hydroxide and their dissol-  
1024 ution in a small volume of nitric acid solution.  
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### 1026 2.12. Ammonia

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1029 A FI on-line filterless precipitation–dissolution system for the FAAS  
1030 determination of trace lead in water samples was described by Yan et al.<sup>[60]</sup>  
1031 On-line precipitation of trace Pb was achieved by merging the sample solution  
1032 with an NH<sub>3</sub> solution. The resultant precipitates were collected onto the inner  
1033 walls of the KR without filtration. A flow of nitric acid was introduced to dis-  
1034 solve the precipitates and to deliver the analyte for online FAAS detection.  
1035 With the proposed methodology the concentration of lead in a certified refer-  
1036 ence material (GBW 08607, River Water) was  $0.96 \pm 0.04 \mu\text{g g}^{-1}$  using  
1037 simple aqueous standards for calibration. These results were in good agree-  
1038 ment with the certified value. This method was successfully applied to the  
1039 determination of trace lead in a variety of real water samples.

1040 A fully automated FI on-line filterless precipitation–dissolution system  
1041 developed for ICP-MS determination of (ultra)trace REE in environmental  
1042 and geological samples have been described by Yan and co-workers.<sup>[61]</sup> A  
1043 PTFE KR was used as a filterless collector. On-line precipitation of REE  
1044 was achieved by mixing the sample with an ammonia buffer solution. The  
1045 resulting precipitates were collected on the inner walls of the KR without  
1046 filtration. A flow of diluted nitric acid was introduced to dissolve the collected  
1047 precipitates and to transport the analyte to the ICP-MS system. Group REE  
1048 preconcentration was achieved with separation from alkali and alkaline  
1049 earth elements at pH 8.3–9.0. The accuracy of the method was demonstrated  
1050 by analyzing a number of geological and environmental standard reference

1051 materials. The method was also applied to determination of ultra-trace REE in  
1052 porewater samples.

1053 Burguera and co-workers<sup>[62]</sup> have developed a work for the determination  
1054 of beryllium in natural and waste waters using on-line FI preconcentration by  
1055 precipitation–dissolution with the ETAAS determination. Beryllium was pre-  
1056 cipitated quantitatively with  $\text{NH}_4\text{OH}-\text{NH}_4\text{Cl}$  and collected in a knotted tube  
1057 of Tygon without using a filter. The precipitate was dissolved with nitric acid  
1058 and a sub-sample was collected in a capillary of a sampling arm assembly, to  
1059 introduce 10  $\mu\text{L}$  volumes into the graphite tube by means of positive displace-  
1060 ment with air through a time-based injector. The detection limit (3 sec) of  
1061 25  $\text{ng L}^{-1}$  in the sample solution was obtained. The integrated system  
1062 permits fully automated operation, avoiding time-consuming manual work,  
1063 and enhancing the reproducibility and precision of the determination of beryl-  
1064 lium. The results obtained for the determination of beryllium in certified refer-  
1065 ence materials demonstrate the applicability of the procedure to the analysis of  
1066 natural waters.

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### 2.13. 1-Phenyl-3-methyl-4-benzoylpyrazol-5-one

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1072 A new scheme was developed for the FI on-line sorption preconcentration  
1073 of copper and manganese in a KR precoated with the chelating reagent  
1-phenyl-3-methyl-4-benzoylpyrazol-5-one by Benkhedda and co-workers.<sup>[63]</sup>

1074 This system offers several advantages in comparison with the conventional  
1075 preconcentration scheme involving on-line merging of the sample and chela-  
1076 ting reagent solution: higher sensitivity owing to the more favorable condi-  
1077 tions of analyte preconcentration on the “immobilized” reagent, better  
1078 optimization of the separated processes of reagent sorption on the KR and  
1079 analyte preconcentration, no analyte losses due to adsorption of chelate com-  
1080 plexes on the tubing outside the KR and no need of a prefill step between  
1081 samples of different analyte concentration. The chelating reagent 1-phenyl-  
1082 3-methyl-4-benzoylpyrazol-5-one was chosen due to it forms complexes  
1083 with more than 40 metal ions and has found numerous applications in trace  
1084 element separation and preconcentration by solvent extraction. This is the  
1085 first work in which this reagent was used for FI on-line sorption preconcentra-  
1086 tion. The accuracy of the method was demonstrated by the analysis of certified  
1087 reference materials.

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Likewise, Benkhedda and co-workers<sup>[64]</sup> have reported a FI on-line sorp-  
tion system, for the preconcentration and separation in a KR coupled with  
ICP-TOFMS for the fast, selective, and sensitive determination of ultra-  
trace concentrations of rare earth elements in environmental waters. The on-  
line preconcentration and separation of the REEs is achieved by sorption of

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1093 the REE complexes formed on the inner walls of a PTFE KR precoated with  
1094 the chelating reagent PMBP at a pH of 9.6. The analytes were eluted and trans-  
1095 ported to the ICP-TOFMS system with HNO<sub>3</sub>, using ultrasonic nebulization.  
1096 The REEs are effectively preconcentrated and separated from the major  
1097 matrix constituents—alkali and alkaline earth elements. The stable and reliable  
1098 operation of the preconcentration system may be related to the practically  
1099 unlimited lifetime of the KR. Using ICP-TOFMS as a detector for FI analysis,  
1100 22 isotopes were simultaneously measured in a transient peak without affect-  
1101 ing the time of analysis, which is mainly determined by the duration of the  
1102 preconcentration process.

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**3. CONCLUSIONS**

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**ACKNOWLEDGMENTS**

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