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Review

Complex-forming organic ligands in cloud-point extraction of metal ions: A review

K. Pytlakowska *, V. Kozik, M. Dabioch

Institute of Chemistry, University of Silesia, ul. Szkolna 9, 40-006 Katowice, Poland

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ABSTRACT

Cloud-point extraction (CPE), an easy, safe, environmentally friendly, rapid and inexpensive methodology for preconcentration and separation of trace metals from aqueous solutions has recently become an attractive area of research and an alternative to liquid–liquid extraction. Moreover, it provides results comparable to those obtained with other separation techniques and has a greater potential to be explored in improving detection limits and other analytical characteristics over other methods. A few reviews have been published covering different aspects of the CPE procedure and its relevant applications, such as the phenomenon of clouding, the application in the extraction of trace inorganic and organic materials, as well as pesticides and protein substrates from different sources, or incorporation of CPE into an FIA system. This review focuses on general properties of the most frequently used organic ligands in cloud-point extraction and on literature data (from 2000 to 2012) concerning the use of modern techniques in determination of metal ions' content in various materials. The article is divided according to the class of organic ligands to be used in CPE.

Contents

Abbreviations: 5-Br-PADAP, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol; PAN, 1-(2-pyridylazo)-2-naphthol; PAR, 4-(2-pyridylazo)resorcinol; TAN, 1-(2-thiazolylazo)-2-naphthol; TAR, 4-(2-thiazolylazo)resorcinol; TAC, 2-(2′-thiazolylazo)-*p*-cresol; BDAP, 2-(2′-benzothiazolylazo)-5-(*N*,*N*-diethyl)aminophenol; MBT, 2-mercaptobenzothiazole; Br-TAO, 4-(5-bromo-2-thiazolylazo)orcinol; Me-BTABr, 2-[2′-(6-methyl-benzothiazolylazo)]-4-bromophenol; Br-TACl, 2-(5-bromothiazolylazo)-4-chlorophenol; APDC, ammonium pyrrolidine dithiocarbamate; DDTC, diethylammonium-N,N′-diethyldithiocarbamate; 8-HQ, 8-hydroxyquinoline; DDTP, ammonium O,O-diethyldithiophosphate; TMK, 4,4′-bis(dimethylamino) thiobenzophenone, e.g. Thio-Michler's Ketone; morin, 3,5,7,2′-4′ pentahydroxy flavone; BPHA, N-benzoyl-N-phenyhydroxylamine; ACDA, 2-amino-cyclopentene-1-dithiocarboxylic acid; PMBP, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone; HEPTS, 4-ethyl-1-(pyridin-2-yl)thiosemicarbazide; HDEHP, di(2-ethylhexyl)phosphoric acid; NDDBH, 6-(4-nitrophenyl)–2,4-diphenyl–3,5-diaza-bicyclo[3.1.0]hex–2-ene; THF, tetrahydrofuran; DMF, dimethylfuran; BDTAC, benzyldimethyltetradecylammonium chloride; CTAB, cetyltrimethylammonium bromide; CPC, cetyl pyridinium chloride; SDS, sodium dodecyl sulfate; FAAS, flame atomic absorption spectrometry; ETAAS, electrothermal atomic absorption spectrometry; GFAAS, graphite furnace atomic absorption spectrometry; CVAAS, cold vapor atomic absorption spectrometry; HGAAS, hydride generation atomic absorption spectrometry; TS-FF-AAS, thermospray flame furnace atomic absorption spectrometer; ICP-OES, inductively coupled plasma optical emission spectrometry; ICP-MS, inductively coupled plasma mass spectrometry; ETV-ICP-OES, electrothermal vaporization inductively coupled plasma atomic emission spectrometry; USN-ICP-OES, inductively coupled plasma optical emission spectrometry with ultrasonic nebulization; CV-ICP-OES, cold vapour optical emission spectrometry; ETV-ICP-MS, electrothermal vaporization inductively coupled plasma mass spectrometry; ICP-DRC-MS, inductively coupled plasma mass spectrometry with dynamic reaction cell; SPF, spectrofluorimetry; CVAFS, cold vapor atomic fluorescence spectrometer; ETVAFS, electrothermal vaporization flame atomic fluorescence spectrometry; TLS, thermal lens spectrometry; FO-LADS, fiber optic-linear array detection spectrophotometry; CE, capillary electrophoresis; NAA, neutron activation analysis; HPLC, high-performance liquid chromatography

* Corresponding author. Tel.: +48 32 3591246; fax: +48 32 2599978.
E-mail address: katarzyna.pytlakowska@us.edu.pl (K. Pytlakowska).

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1. Introduction

Determination of trace amounts of metals in a complex matrix has been usually complicated, despite modern analytical instrumentation now available, even with adequate sensitivity. In such matrixes, determination should be preceeded by separation and preconcentration steps. This enables minimizing or even eliminating matrix effects and contaminants, lowering the detection limit of many metals with different techniques and enhancing the detectability for others. Thanks to green chemistry concept, modern analytical separation/preconcentration procedures should be simple, ecologically safe, sensitive, and selective for microcomponents' determination, combining concentration and further determination by physical or physico–chemical methods. Several strategies were adopted aiming at greener analytical procedures, involving replacement of toxic reagents, minimized reagent consumption, recycling and waste treatment. One of them is the use of surfactants, due to their low toxicity and relatively low cost. Moreover, interest in application of surfactants is related to their unique microheterogeneous structures capable of selective interaction with different solute molecules which can strongly modify solubility, chemical equilibrium, kinetics and the spectroscopic properties of analytes and reagents. Therefore, in the last few decades, development has been observed concerning surfactant-based methods in many chemical and pharmaceutical fields, organic synthesis and several industrial applications. Micellar systems are also widely utilized in analytical chemistry, especially in separation/preconcentration procedures and determination based on spectral methods.

Aqueous solutions of many non-ionic and zwitterionic surfactant micellar systems become turbid over a narrow temperature range, when the experimental conditions have been changed. This temperature is named "cloud point temperature" (CPT) or "lower consolute temperature" (LCT). The value of CPT depends on the structure and concentration of the surfactant, and the presence of additives such as salts, alcohols, other surfactants, polymers, and some organic or inorganic compounds, which can cause an increase or decrease of CPT. Therefore, in micellar systems two types of phase separation can be observed: upper consolute type (occurring above CPT) and lower consolute type (occurring below CPT). The lower consolute type of phase separation is rarely obtained in micellar systems. Nevertheless, in some cases the cloud point was attained below CPT and even at room temperature, by changing pressure or using various additives, including electrolytes [1–4]. In micellar media, the upper consolute type of phase separation dominates. In this case, clouding phenomenon is observed especially with polyoxyethylene surfactants and can be ascribed to the efficient dehydration of hydrophilic portion of micelles at higher temperature conditions, and due to the interaction of nonionic surfactant micelles via an attractive potential, whose well-depth increases with temperature. These micelles attract each other and form clusters with the approach of the cloud point. However, the mechanism behind the lower consolute behavior of nonionic surfactant systems still remains obscure. Earlier, the phase separation was attributed to the micellar growth, the micellar coacervation, or the changes in poly (oxyethylene) chain conformations with temperature. However, recent experimental and theoretical investigations put forth the view that the formation of the connected micellar network or the strongly orientation-dependent interactions (H bonds) between water and the surfactant molecules could be responsible for the lower consolute behavior. Moreover, the roles of oscillation in the critical concentration, and of micellar growth as mechanisms for the clouding phenomenon are still controversial [5–7]. More details about the clouding behavior of ionic and nonionic surfactants and influence of different kinds of additives on CPT can be found in reviews by Mukherjee et al. and Bezerra et al. [7,8].

Clouding behavior of micellar solutions is widely exploited as CPE for the extraction and preconcentration of various metal ions, organic and inorganic industrial pollutants, pesticides and proteins. The typical cloud point methodology used for extraction of metal ions is given in Fig. 1.

Cloud point extraction (CPE), as an effective separation/preconcentration technique, first studied by Watanabe and coworkers in the early 1980s [9–12], has been demonstrated to have the distinct merits of low cost, simplicity, speed, lower toxicity to the environment than extractions that use organic solvents and a high capacity to concentrate a wide variety of analytes of widely varying nature with high recoveries and high concentration factors. On the other hand, simple combination with spectral, atomic absorption, chromatographic, and electrochemical analyses allows using cloud-point extraction for elaborating high-sensitive and convenient analytical methods. The frequency of use of analytical techniques combined with CPE that were proposed in the past 12 years is given in Fig. 2. As can be seen, flame atomic absorption spectrometry (FAAS) is by far the most widely employed technique for analyte determination, followed by CPE preconcentration. FAAS has been a very attractive technique for routine metal determinations due to well-known interferences, its ease of operation, its low acquisition and operating costs compared with electrothermal atomic absorption spectrometry (ETAAS), graphite furnace atomic absorption spectrometry (GFAAS) or inductively coupled plasma mass spectrometry (ICP-MS), and its high sample throughput.

In the CPE technique, surfactant is one of the key reagents. The surfactants which are used in cloud point extraction are mostly of nonionic type, such as Triton X-114 (polyoxyethylene-7.5-octylphenoxy ether), Triton X-100 (polyoxyethylene-9.5-octylphenoxy ether) or PONPE (polynonylphenyl ether). In some cases, mixtures of nonionic and cationic/anionic (CTAB, CPC, BDTAC, and SDS)

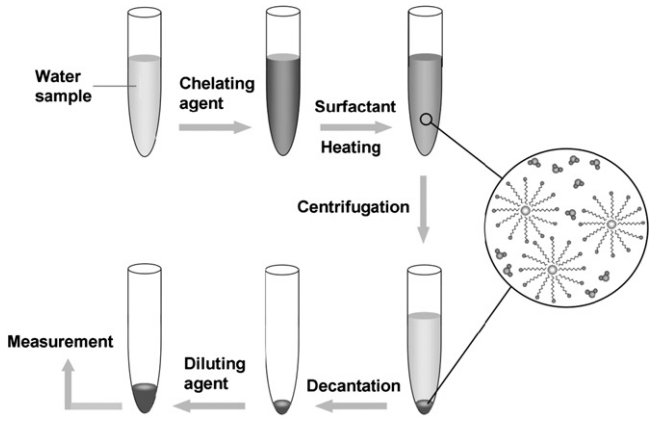


Fig. 1. Schematic representation of a conventional CPE to metal preconcentration.

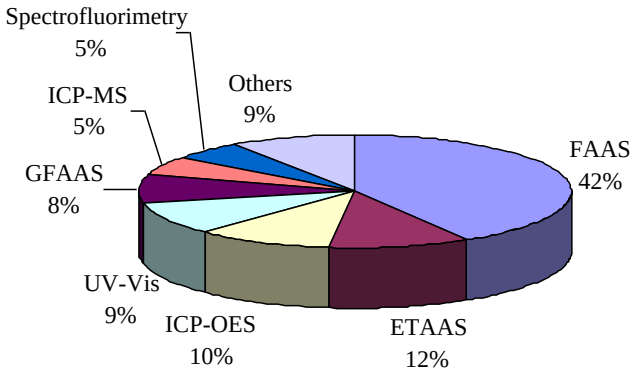


Fig. 2. Frequency of use of analytical techniques combined with CPE proposed in the past 12 years.

surfactants or only cationic surfactants (CTAB, and CPC) are also applied. The use of cationic surfactants in combination with a non-ionic surfactant has been documented with an increase in the extraction efficiency of polar compounds. On the other hand, application of only cationic surfactant in CPE requires high salt concentration. In this case, phase separation is typically of the upper consolute type, i.e., it occurs on cooling below a characteristic temperature (CPT) which, in turn, increases with salt content. The frequency of use of different surfactants in CPE is given in Fig. 3. As can be seen, among the many kinds of surfactants, Triton X-114 has been the most applied reagent because of its low cloud-point temperature (30 °C) and high density of the surfactant rich phase, as well as low cost, commercial availability and lower toxicity. Triton X-100 was less frequently considered and employed, for its higher CPT (65 °C) made it more difficult to turn the solution turbid and attain high extraction efficiency.

Extraction of metal ions by CPE can be performed in the absence of a chelating agent but according to available literature data only a few ligandless CPE methods were proposed [13–27]. Metal ions' separation is significantly improved by the formation of insoluble or sparingly water-soluble complexes which have hydrophobic properties. In such cases, the efficiency of the CPE depends on the hydrophobicity of the ligand and the complex, their apparent equilibrium constants in the micellar medium and kinetics of the complex formation and their transference between the phases. Among various organic ligands used in cloud point extraction, pyridylazo and thiazolylazo derivatives, such as 1-(2-pyridylazo)-2-naphthol (PAN), 1-(2-thiazolyazo)-2-naphthol (TAN), 4-(2-pyridylazo)resorcinol (PAR), and 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (5-Br-PADAP) have been widely employed due to their low solubility in water and capacity to form complexes with a large variety of metals. Other reagents used for cloud point extraction in several procedures are ammonium pyrrolidinedithiocarbamate (APDC), diethyldithiocarbamate (DDTC), 2-amino-cyclopentene-1-dithiocarboxylic acid (ACDA), O,O-diethyldithiophosphate (DDTP), 8-hydroxyquinoline (oxine, 8-HQ), and dithizone. The main groups of ligands mostly used in CPE preconcentration would be outlined in this paper.

The papers reviewed in here include those that appeared between 2000 and 2012. However, other reviews focusing on the cloud-point extraction should also be mentioned here. The theory and relevant applications of the cloud-point extraction are discussed in various reviews [8,28–33]. Three recent (and very interesting) reviews have been published covering different aspects of the CPE procedure and their application to metal determinations. Mukherjee et al. [7] discussed the phenomenon of clouding and the applications of cloud point technology in the extraction of trace inorganic and organic materials, as well as pesticides and protein substrates from different sources. Bosch Ojeda and Sánchez Rojas reviewed the application of CPE in determination of metal ions, listed in alphabetical order, over the period between 2004 and 2008 [34], and 2009 to the first part of 2011 [35]. They also discussed incorporation of CPE into a FIA system. Khammas [36] presented various aspects of micelle-mediated extraction in metal and organic analyses, such as the principle and theoretical aspects of the CPE and its analytical application as an initial step before determination of metal ions by atomic spectrometry as well as biochemical and organic molecules in different matrices.

This review surveys characteristics of organic ligands most frequently used in cloud-point extraction and literature data (from 2000 to 2012) related to determination of metal ions in various materials by using modern techniques. The article is divided according to the class of ligands to be used in CPE.

2. Azo dyes in CPE

Among complexing reagents that have been widely employed for cloud point extraction, the azo dyes deserve special attention due to their capacity to form mostly neutral and hydrophobic complexes with the vast majority of transition metals.

Azo reagents represent the largest and most important group of synthetic dyes which are found in a variety of industrial applications mainly due to their color fastness and low price. Their basic structure is Ar–N═N–Ar′, where Ar and Ar′ designate any aromatic groups. The unit that contains the bond –N═N– is referred to as the azo group and is a chromophore that gives brilliant color to these compounds. Therefore, they are widely used for coloring numerous consumer goods, such as leather, clothes, food, toys, plastics and cosmetics [37].

In analytical chemistry, they play an important role as organic complexing reagents. These dyes are considered as tridentate ligands and form chelates with metal ions through oxygen atom of the ortho-hydroxyl group, nitrogen atom from pyridine, and one of nitrogen atoms of azo group, giving two 5-membered chelate rings (Fig. 4).

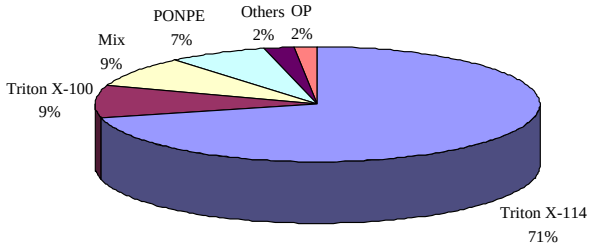


Fig. 3. Frequency of use of surfactants in CPE proposed in the past 12 years.

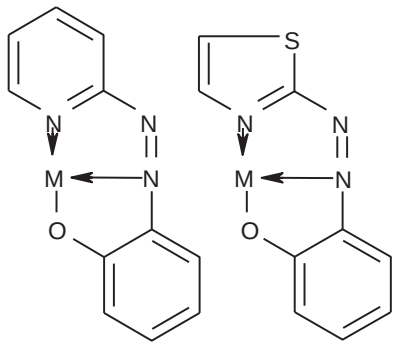


Fig. 4. Structure of the azo dye complexes.

The complexes are stable with rather limited solubility in aqueous solution but much greater solubility in organic system. Because of their non-selectivity, azo dyes have been widely applied in different areas of analytical chemistry such as the spectrophotometry, SPE, LC, electrochemistry, liquid–liquid extraction and CPE [38–41]. They are also employed as indicators in complexometric titrations. Moreover, according to the pH of the solution, they can exist in three different structural prototropic forms and the color of these charged species is found to change with the variation in hydrogen-ion concentration. Therefore, due to their sensitivity to changes in acidity of solution, they are also used as indicators in alkacymetric titrations. The dissociation constants of the most frequently used azo compounds are shown in Table 1.

Azo dyes are divided into two groups: pyridylazo-dyes with a PAN-type chelating structure and thiazolylazo with a TAN-type chelating structure.

2.1. Pyridylazo dyes in CPE

Pyridylazo compounds have been widely applied as chromogenic reagents in spectrophotometry for the determination of metallic elements, including iron, cobalt, nickel, copper, zinc, chromium, palladium, mercury and cadmium, as well as organic substances, such as nucleic acids and tartaric acid. Additionally, the reactions of pyridylazo reagents with metallic ions have been used in procedures involving atomic spectrometry, chromatography and electroanalytical techniques in order to increase the sensitivity and the selectivity of the analysis [39,45].

These dyes act as tridentate ligands complexing with most metals through the ortho-hydroxyl group, the azo nitrogen

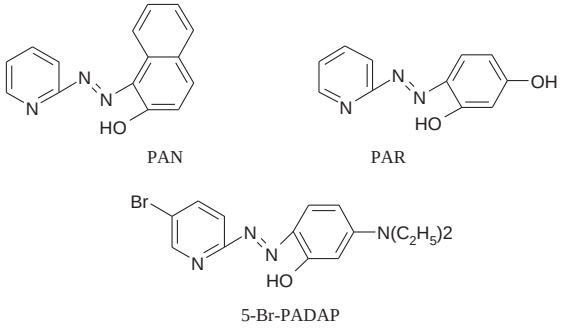


Fig. 5. Structure of pyridylazo compounds most frequently applied in CPE.

Table 1
Dissociation constants of the most frequently used azo compounds.

Azo compound	Dissociation constants pK_a			Conditions	Ref.
1-(2-pyridylazo)-2-naphthol (PAN)	$pK_{NH}<2$	$pK_{OH}=12.3$			[42]
2-(5-bromo-2-pyridylazo)-5-diethilaminophenol (5-Br-PADAP)	$pK_{a1}=0.1$	$pK_{a2}=2.02$	$pK_{a3}=11.3$		[43]
4-(2-pyridylazo)resorcinol (PAR)	$pK_{NH}=2.7$	$pK_{p\text{-}OH}=5.83$	$pK_{o\text{-}OH}=12.5$	0.1 mol L^{-1} KNO_3	[42,44]
	$pK_{NH}=2.66$	$pK_{p\text{-}OH}=5.48$	$pK_{o\text{-}OH}=12.31$	0.1 mol L^{-1} $NaClO_4$	
	$pK_{NH}=3.1$	$pK_{p\text{-}OH}=5.6$	$pK_{o\text{-}OH}=11.9$	$I=0.1$	
	$pK_{NH}=2.57$	$pK_{p-OH}=6.2$	$pK_{o\text{-}OH}=11.5$		
	$pK_{NH}=3.03$	$pK_{p\text{-}OH}=5.57$	$pK_{o\text{-}OH}=11.95$	$I=0.1$	
	$pK_{NH}=3.02$	$pK_{p\text{-}OH}=5.56$	$pK_{o\text{-}OH}=11.98$	0.1 mol L^{-1} KNO_3	
	$pK_{NH}=2.3$	$pK_{p\text{-}OH}=6.9$	$pK_{o\text{-}OH}=12.4$	$I<0.01$, 50% dioxane	
	$pK_{NH}=2.35$	$pK_{p\text{-}OH}=7.01$	$pK_{o\text{-}OH}=13.0$	$I=0.1$, 50% dioxane	
	$pK_{NH}=2.31$	$pK_{p\text{-}OH}=6.87$	$pK_{o\text{-}OH}=13.42$	$I=0.01$, 50% dioxane	
	$pK_{NH}=2.49$	$pK_{p\text{-}OH}=6.54$	$pK_{o\text{-}OH}=12.36$	50% Dioxane	
	$pK_{NH}=2.93$	$pK_{p\text{-}OH}=6.81$	$pK_{o\text{-}OH}=12.12$	$I=0.06$, 50% ethanol	
	$pK_{NH}=2.64$	$pK_{p\text{-}OH}=-$	$pK_{o\text{-}OH}=5.9$	30% DMF	
1-(2-thiazolylazo)-2-naphtol (TAN)	$pK_{NH}=-$	$pK_{COOH}=-$	$pK_{OH}=8.94$	20% Acetone	[39]
	$pK_{NH}=2.37$	$pK_{COOH}=-$	$pK_{OH}=8.71$	Water	
	$pK_{NH}=1.72$	$pK_{COOH}=-$	$pK_{OH}=8.94$	30% Acetone	
2-(2-thiazolylazo)-*p*-cresol (TAC)	$pK_{NH}=-$	$pK_{p\text{-}OH}=-$	$pK_{o\text{-}OH}=8.95$	50% Methanol	[39]
	$pK_{NH}=0.4$	$pK_{p\text{-}OH}=-$	$pK_{o\text{-}OH}=8.31$	10% Dioxane	
	$pK_{NH}=-$	$pK_{p\text{-}OH}=-$	$pK_{o\text{-}OH}=8.36$	Water–dioxane	
4-(2-thiazolylazo) resorcinol (TAR)	$pK_{NH}=1.25$	$pK_{p\text{-}OH}=6.0$	$pK_{o\text{-}OH}=9.3$	0.1 mol L^{-1} $NaClO_4$	[44]
	$pK_{NH}=0.96$	$pK_{p\text{-}OH}=6.23$	$pK_{o\text{-}OH}=9.44$	0.1 mol L^{-1} $NaClO_4$	
	$pK_{NH}=-$	$pK_{p\text{-}OH}=6.16$	$pK_{o\text{-}OH}=9.59$	$I=0.2$	
	$pK_{NH}=-$	$pK_{p\text{-}OH}=6.15$	$pK_{o\text{-}OH}=9.68$		
	$pK_{NH}=1.56$	$pK_{p\text{-}OH}=-$	$pK_{o\text{-}OH}=-$	$I=1.0$	
	$pK_{NH}=-$	$pK_{p\text{-}OH}=-$	$pK_{o\text{-}OH}=9.15$	0.1 mol L^{-1} $NaClO_4$	
	$pK_{NH}=-$	$pK_{p\text{-}OH}=5.9$	$pK_{o\text{-}OH}=10.3$	Water	
	$pK_{NH}=-$	$pK_{p\text{-}OH}=6.4$	$pK_{o\text{-}OH}=10.52$	20% Methanol	
	$pK_{NH}=1.13$	$pK_{p\text{-}OH}=6.18$	$pK_{o\text{-}OH}=9.88$	$I=0.1$, 2% dioxane	
	$pK_{NH}=0.98$	$pK_{p\text{-}OH}=6.17$	$pK_{o\text{-}OH}=9.49$	$I=0.1$, 2% dioxane	
	$pK_{NH}=1.65$	$pK_{p\text{-}OH}=7.37$	$pK_{o\text{-}OH}=12.80$	$I<0.01$, 50% dioxane	
	$pK_{NH}=0.9$	$pK_{p\text{-}OH}=6.53$	$pK_{o\text{-}OH}=10.76$	$I=0.1$, 50% methanol	
	$pK_{NH}=-$	$pK_{p\text{-}OH}=5.9$	$pK_{o\text{-}OH}=10.3$	20% Methanol	
	$pK_{NH}=-$	$pK_{p\text{-}OH}=6.5$	$pK_{o\text{-}OH}=10.7$	50% Methanol	
	$pK_{NH}=-$	$pK_{p\text{-}OH}=6.2$	$pK_{o\text{-}OH}=9.4$	5% Ethanol	
	$pK_{NH}=0.75$	$pK_{p\text{-}OH}=6.51$	$pK_{o\text{-}OH}=10.67$	0.1 mol L^{-1} KNO_3 30% Ethanol	
	$pK_{NH}=0.75$	$pK_{p\text{-}OH}=6.56$	$pK_{o\text{-}OH}=10.54$	$I=0.1$, 30% ethanol	
	$pK_{NH}=0.84$	$pK_{p\text{-}OH}=6.56$	$pK_{o\text{-}OH}=10.42$	1 mol L^{-1} $NaClO_4$ 30% DMF	
	$pK_{NH}=1.06$	$pK_{p\text{-}OH}=7.25$	$pK_{o\text{-}OH}=11.52$	1 mol L^{-1} $NaClO_4$ 50% DMF	

Table 2
Pyridylazo dyes used in CPE.

Ion	Reagent	Micellar system	SRP diluting agent	Detection system	DL	Linearity	PF	Matrix	Ref.
Hg	5-Br-PADAP	PONPE 5	HNO_3 in ethanol	ICP-OES	4 ng L^{-1}	At levels near DLs up 50 μg L^{-1}	200	Tap water	[48]
V	5-Br-PADAP	PONPE 5	Ethanol	ICP-OES	16 ng L^{-1}	At levels near DLs up to 50 μg L^{-1}	250	Parenteral solutions	[49]
Co	5-Br-PADAP	Triton X-100 and SDS with separation induced by HCl (1) or NaCl (2)	0.1 mol L^{-1} HCl in ethanol	FAAS	1.1 μg L^{-1} (1) 1.6 μg L^{-1} (2)	25–200 μg L^{-1}	28,5 (1) 21.7 (2)	Tablets	[4]
Dy	5-Br-PADAP	PONPE-7.5	4 mol L^{-1} HNO_3	ICP-OES	0.03 μg L^{-1}	At levels near DLs up to at least 100 μg L^{-1}	50	Urine samples	[50]
Al	5-Br-PADAP	Triton X-114	1% HNO_3 in methanol	FAAS	0.2 μg L^{-1}	0.7–60 μg L^{-1}	74	Saline effluents from oil refinery samples	[51]
Dy, Fe	5-Br-PADAP	PONPE 7.5	Acetonitrile	CE	0.20 μg L^{-1} Dy, 0.48 μg L^{-1} Fe	At levels near DLs up to at least 500 μg L^{-1}	200	Urine samples	[52]
Pb	5-Br-PADAP	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	GFAAS	0.08 μg L^{-1}	At levels near DLs up to at least 30 μg L^{-1}	50	Tap, underground, river water	[53]
U	5-Br-PADAP	Triton X-114	Ethanol	Spectrophotometry	0.15 μg L^{-1}	0.5–30 μg L^{-1}	50.4	Water from uranium mine	[54]
Cd	5-Br-PADAP	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	GFAAS	0.04 μg L^{-1}		21	Tap, river and underground water	[55]
Cd	5-Br-PADAP	PONPE 7.5	0.1 mo L^{-1} HNO_3 in methanol	ETAAS	0.008 μg L^{-1}	At levels near to DLs up to 1 μg L^{-1}	22	Urine, water	[56]
Hg	5-Br-PADAP	PONPE 7.5	0.1 mol L^{-1} HNO_3 in methanol	ETAAS	0.01 μg L^{-1}	At levels near to DLs up to 16 μg L^{-1}	22	Human hair; urine, water	[57]
Fe	5-Br-PADAP	Triton X-114	Ethanol	Spectrophotometry	0.8 μg L^{-1} Fe(II) 1 μg L^{-1} Fe(III)	5–112 μg L^{-1}	20	Beer	[58]
Cr, Co	5-Br-PADAP	Triton X-114	HNO_3 (1+1)	GFAAS	23 ng L^{-1} Cr 12 ng L^{-1} Co	0.25–2 μg L^{-1} Cr 0.25–5 μg L^{-1} Co	26.2 Cr 41 Co	Vegetal leaves of orange tree (*Citrus sinensis*), alfalfa (*Medicago sativa L.*), apple tree leaves	[59]
Ga, In	5-Br-PADAP	Triton X-100		ICP-OES	0.72 ng mL^{-1} Ga 0.28 ng mL^{-1} In	6–200 ng mL^{-1} Ga 2–200 ng mL^{-1} In		Urine, lake water	[60]
Zn	5-Br-PADAP	OP		FAAS	4.93×10^{-3} μg mL^{-1}	5.0×10^{-3}–0.5 μg mL^{-1}	25	Soil samples	[61]
Cd, Co Cr, Cu Mn, Ni Pb, Zn	PAN (1) 5-Br-PADAP (2)	Triton X-114	HNO_3	ICP-OES	4.0 μg L^{-1} Cd (1) 5.3 μg L^{-1} Cd (2) 4.6 μg L^{-1} Co (1) 4.3 μg L^{-1} Co (2) 2.1 μg L^{-1} Cr (1) 2.5 μg L^{-1} Cr (2) 1.9 μg L^{-1} Cu (1) 2.6 μg L^{-1} Cu (2) 0.3 μg L^{-1} Mn (1) 0.7 μg L^{-1} Mn (2) 5.6 μg L^{-1} Ni (1) 14 μg L^{-1} Ni (2) 69 μg L^{-1} Pb (1) 40 μg L^{-1} Pb (2) 2.0 μg L^{-1} Zn (1) 4.7 μg L^{-1} Zn (2)	20–500 μg L^{-1} Cd (1) 15–500 μg L^{-1} Cd (2) 15–300 μg L^{-1} Co (1,2) 15–1000 μg L^{-1} Cr (1) 10–1000 μg L^{-1} Cr (2) 10–500 μg L^{-1} Cu (1) 15–500 μg L^{-1} Cu (2) 2–1000 μg L^{-1} Mn (1,2) 40–400 μg L^{-1} Ni (1) 20–400 μg L^{-1} Ni (2) 100–5000 μg L^{-1} Pb (1,2) 20–5000 μg L^{-1} Zn (1) 40–5000 μg L^{-1} Zn (2)	13	Dolomite and bone ash	[62]
Pb	PAN	Triton X-114	0.5 mol L^{-1} of HNO_3 in ethanol	FAAS	5.27 ng mL^{-1}	7.5 ng mL^{-1}–3.5 μg mL^{-1}	30	Pepperbush, tea leaves, tap, mineral and well water	[63]
Co	PAN	Triton X-114	Methanol	FAAS	0.38 μg L^{-1}	1–120 μg L^{-1}	115	Urine samples	[64]
Mn	PAN	OP-7	Water	FAAS	5 μg L^{-1}		20	River and lake water	[65]
Zn, Co, Ni	PAN	Triton X-114	Ethanol	Spectrophotometry		2–150 ng mL^{-1} Zn 5–250 ng mL^{-1} Co 2–150 ng mL^{-1} Ni	20	Tap water and urine	[66]
Mn	PAN	Triton X-114	Methanol	FAAS	0.39 ng mL^{-1}	1.02–142 ng mL^{-1}	49.1	River water and cow milk	[67]
Co	PAN	Triton X-114	Carbon tetrachloride	TLS	0.03 ng mL^{-1}	0.2–40 ng mL^{-1}	470	Tap, river and sea water	[68]

Cd	PAN	Triton X-100	2 mol L^{-1} HCl	GFAAS	5.9 ng L^{-1}	0–20.0 ng mL^{-1}	50	Tap water	[69]
Co, Ni	PAN	Triton X-114	Ethanol	FO-LADS	0.2 μg L^{-1} Co 0.04 μg L^{-1} Ni	0.6–30.0 μg L^{-1} Co 0.1–15.0 μg L^{-1} Ni	198 Co 199 Ni	Tap, river, dispenser water, serum	[70]
Rh	PAN	Triton X-114	Carbon tetrachloride	TLS	0.06 ng mL^{-1}	0.5–50 ng mL^{-1}	450	Tap, drinking, sea and dispenser water	[71]
Hg	PAN	Triton X-114	L-cysteine	CE	45.2 μg L^{-1} EtHg 47.5 μg L^{-1} MeHg 4.1 μg L^{-1} PhHg 10 μg L^{-1} Hg(II)		17 EtHg 15 MeHg 45 PhHg 52 Hg(II)	Lake and river water, tilapia muscle	[72]
Cu, Zn	PAN	Triton X-114	1% HNO_3 in methanol	FAAS	0.1 μg L^{-1} Cu 0.15 μg L^{-1} Zn	10–50 μg L^{-1} Cu 10–50 μg L^{-1} Zn	36 Cu 32 Zn	Oats, powdered chocolate, corn flour and wheat flour, corn bran and whole meal flour	[73]
V	PAN	Triton X-100	0.1 mol L^{-1} HNO_3 in methanol	FAAS	0.6 μg L^{-1}	10–120 μg L^{-1}	33	Sea, lake and river water	[74]
Cr	PAN	Triton X-114	1% HNO_3 in ethanol	FAAS	0.7 μg L^{-1}	2.5–80 μg L^{-1}	48	River water	[75]
Pd	PAN	Triton X-114	Carbon tetrachloride	TLS	0.04 ng mL^{-1}	0.3–60 ng mL^{-1}	460	Tap, drinking, dispenser, sea water	[76]
Al	PAN	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	GFAAS	0.06 ng mL^{-1}	Up to 20 ng mL^{-1}	34.8	Human albumin samples	[77]
Zn	PAN	Triton X-114	0.1 mol L^{-1} HNO_3 in ethanol	FAAS	1.52 μg L^{-1}	5–20 μg L^{-1}	26	Medicinal plants. human blood	[78]
Pd, Au, Ni	PAN	Triton X-114	1 mol L^{-1} HNO_3	FAAS	3.4 ng mL^{-1} Pd 3.9 ng mL^{-1} Au 2.4 ng mL^{-1} Ni	0.01–1.0 μg L^{-1} Pd 0.01–1.5 μg L^{-1} Au 0.01–0.5 μg L^{-1} Ni		River water	[79]
Cd	PAN	Triton X-114	0.1 mol L^{-1} HNO_3 in ethanol	TS-FF-AAS	0.0178 μg L^{-1}	0.1–5 μg L^{-1}	55.5	Soft drinks	[80]
Sn	PAN	Triton X-100 and SDS	2 mol L^{-1} HNO_3	GFAAS	0.51 ng L^{-1}	0–5 μg L^{-1}	50	Tap and lake water	[81]
Cd, Cu, Pb	PAN	Triton X-114	1% HNO_3 in ethanol	FFAAS	0.025 μg L^{-1} Cd 0.38 μg L^{-1} Cu 0.43 μg L^{-1} Pb	2–10 μg L^{-1} Cd 5–50 μg L^{-1} Cu 5–50 μg L^{-1} Pb	59 Cd 25 Cu 21 Pb	Mineral water	[82]
Hg	PAN	Triton X-114	Ethanol	Spectrophotometry	1.65 μg L^{-1}	10–1000 μg L^{-1}	33.3	River, lake and tap water, dental waste water, chrome plating industry effluent, textile industry effluent	[83]
Cu	PAN	PONPE-7.5		NAA	1.5 ppb		60	Tap water	[84]
Cr	PAN	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	GFAAS	0.02 μg L^{-1}	Up to 20 ng mL^{-1}	83.5	Human serum	[85]
Zn	PAR	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	0.0065 mg L^{-1}	0.01–0.10 mg L^{-1}	18	River, sea, tap and mineral water	[86]
Cu, Zn, Cd, Ni	PAR	Triton X-114	0.5 mol L^{-1} HNO_3 in ethanol	ICP-OES	1.2 μg L^{-1} Cu 1.1 μg L^{-1} Zn 1.0 μg L^{-1} Cd 6.3 μg L^{-1} Ni	10–500 μg L^{-1} Cu 10–700 μg L^{-1} Zn 20–2000 μg L^{-1} Cd 50–2500 μg L^{-1} Ni	9.77 Cu 10.1 Zn 9.36 Cd 9.79 Ni	Drinking, mineral and lake water	[87]

nearest to the phenolic ring and the heterocyclic nitrogen atom, giving two stable, 5-membered chelate rings. They form complexes with ions of small size carrying a large positive charge, such as titanium group (similar to salt-forming reagents) and with ions of heavy metals and transition elements with nearly full d-shells (like other nitrogen-donor chelating agents) [38].

The most frequently used pyridylazo dyes for analytical purpose are: 1-(2-pyridylazo)-2-naphthol (PAN), 2-(5-bromo-2-pyridylazo)-5-diethilaminophenol (5-Br-PADAP), and 4-(2-pyridylazo)resorcinol (PAR) (Fig. 5).

Table 2 summarizes some CPE procedures proposed for metal preconcentration using pyridylazo dyes as complexing ligands, and includes metal ions, reagent, micellar system, surfactant-rich-phase diluting agent, detection limit, linearity, preconcentration factor and matrix data. As can be seen, PAN is the most frequently used pyridylazo ligand compared to others and deserves special attention. PAN was introduced into chemistry by Cheng and Bray [46] in 1955 and since that time it has found wide application in different areas of analytical chemistry due to the fact that it forms inner, mostly reddish colored, water-insoluble chelates with many transition metal ions with metal ion–ligand ratios of 1:1 or 1:2. The complexes of heavy metals form under slightly acid, neutral or alkaline conditions and their stability is greatly affected by the acidity. Moreover, complexing reactions are sensitive to changes in solvent, ionic strength, temperature and concentration of metal and ligand. PAN is rather unselective but it does not form complexes with the alkali and alkaline earth metals, Ge(IV), As, Se and Te [47], thus it may be helpful in determining metal ions in environmental samples. As can be seen in Table 1, in many cases when determining the same elements, PAN gives higher preconcentration factors and lower detection limits than procedures based on 5-Br-PADAP or PAR. Furthermore, the combination of the TLS determination with CPE preconcentration after the formation of complexes with PAN in the presence of Triton X-114 as surfactant, allows to achieve preconcentration factor up to 470 [68], and therefore has a great potential for trace element analysis.

2.2. Thiazolylazo dyes in CPE

Thiazolylazo dyes (2-aminothiazole derivatives) such as 1-(2-thiazolylazo)-2-naphtol (TAN), 2-(2-thiazolylazo)-*p*-cresol (TAC) and 4-(2-thiazolylazo) resorcinol (TAR) (Fig. 6) have been extensively employed for the separation and determination of trace elements. Most of these compounds are only partly soluble in water, and only a few are readily soluble. Nevertheless, their solubility in organic solvents such as chloroform, ethanol, dimethylformamide and acetone is very appreciable. Therefore, they are widely used in extraction-spectrophotometric methods of metal determination, liquid–liquid extraction and cloud-point extraction [40,88].

Thiazolylazo dyes have generally been considered as tridentate ligands towards metal ions. For a thiazolylazo reagent with a hydroxyl group in the ortho position relative to the azo group, the metal ion is bound to the oxygen of the hydroxyl group, the azo group and the nitrogen atom of the thiazole ring forming two five-membered rings [39]. The lower basicity of the thiazole ring causes lower stability of complexes compared to their pyridyl analogs. This in turn means that thiazolylazo dyes are more selective [38].

These dyes give colored complexes with many metals, but stable chelates are formed especially with some of the transition metals. In acidic and slightly acidic solutions, the metals form complexes with a metal to ligand ratio of 1:1 or a mixture of complexes with ratios of 1:1 and 1:2. In alkaline solutions the equilibrium is usually displaced towards the 1:2 complexes [38,39].

In Table 3 we report some CPE methods proposed for metal preconcentration using thiazolylazo dyes as complexing reagents. Compared to pyridylazo dyes, thiazolylazo reagents are less frequently used despite the fact that these compounds have been demonstrated to be promising for trace element analysis due to their good analytical characteristics, such as detection limit, enrichment factor and precision of the proposed procedures.

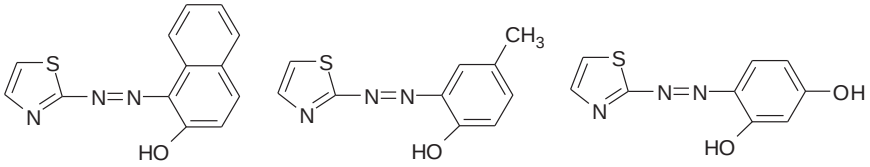
3. Dithiocarbamates

Dithiocarbamates like diethylammonium-N,N′-diethyldithiocarbamate (DDTC) and ammonium pyrrolidine dithiocarbamate (APDC) are the most efficient chelating reagents, next to azo dyes, used in CPE preconcentration of metal ions.

Dithiocarbamates ($R_2CNS_2^-$) are carbamate analogs in which both oxygen atoms are replaced by sulfur atoms. They are a handy class of monoanionic 1,1-dithio ligands widely used in chemistry. They are easily prepared by the reaction of most primary and secondary amines with carbon disulfide and sodium hydroxide.

Dithiocarbamates are highly versatile ligands toward main group metals. They can stabilize a variety of oxidation states and coordination geometries, and seemingly small modifications to the ligand can lead to significant changes in the structure–behavior of the complexes formed [112]. They react with a large number of di- and trivalent metals e.g. Cu(II), Pb(II), Cd(II), Ni(II), Zn(II), Fe(II, III) or Cr(III) which can be separated from a large excess of alkali and alkaline earth elements. This group-specific character makes this chelating reagent ideally suited for the preconcentration of heavy metals from environmental samples including samples of sea water. Moreover, the complex formation is sufficiently rapid; hence it can be adapted to on-line preconcentration and determination systems.

Dithiocarbamates form strong and mostly neutral complexes with the uncommon four-membered ring (Fig. 7). The stability of diethyldithiocarbamate complexes with metals decreases in the following order: Hg, Ag, Co, Cu, Ni, Bi, Pb, Cd, Fe(III), Zn, Mn. The complexes are sparingly soluble in water but dissolve in organic solvents such as carbon tetrachloride, chloroform, amyl acetate or acetone. Carbon tetrachloride extracts the complexes of Bi, Fe, Cu, Ni, Co, Pb; Te; As, Se; and Mn over pH ranges 4–11; 4–9; 4–6; and 6–9 respectively. Complexes of many metals can be extracted into chloroform from fairly strongly acid solutions, e.g. from



TAN TAC TAR

Fig. 6. Structure of thiazolylazo compounds most often applied in CPE.

Table 3
Thiazolylazo dyes used in CPE.

Ion	Reagent	Micellar system	SRP diluting agent	Detection system	DL	Linearity	PF	Matrix	Ref.
Co, Ni	TAN	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	FAAS	0.24 μg L^{-1} Co 0.44 μg L^{-1} Ni	0–120 μg L^{-1} Co 0–130 μg L^{-1} Ni	57 Co 65 Ni	Tap, river and sea water	[89]
Ag	TAN	OP-7	Water	ETAAS		5–250 μg L^{-1}		Mineral water	[90]
Pb, Cd	TAN	Triton X-114	3 mol L^{-1} HCl	FAAS	4.5 μg L^{-1} Pb 0.75 μg L^{-1} Cd	25–2000 μg L^{-1} Pb 2.5–500 μg L^{-1} Cd	15.1 Pb 20.3 Cd	Supply, mineral, lake and river water	[91]
Cr	TAN	Triton X-114	Methanol	HPLC	7.5 μg L^{-1} Cr(III) 3.5 μg L^{-1} Cr(VI)	50–5000 μg L^{-1}	45 Cr(III) 40 Cr(VI)	Lake sediments	[92]
Ni	TAN	Triton X-114	Ethanol	FAAS	5 μg L^{-1}	Up to 80 μg L^{-1}	30	Peach leaves and Apple leaves-CRM	[93]
Mn	TAN	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	FAAS	0.28 ppb	0–120 ppb	57.6	Tap, river, sea and reservoir water	[94]
Zn, Fe	TAN	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	FAAS	1.51 μg L^{-1} Zn 6.45 μg L^{-1} Fe	At levels near DLs up to 100 μg L^{-1} for Zn and 200 μg L^{-1} for Fe	66.4 Zn 70.2 Fe	Human serum and urine	[95]
Mn	TAR	Triton X-114	1% HNO_3 in methanol	FAAS	0.60 μg L^{-1}	1–90 μg L^{-1}	84	Saline effluents of a petroleum refinery	[96]
Hg	TAR	Triton X-114	Ethanol	Spectrophotometry	14.5 μg L^{-1}	50–2500 μg L^{-1}	33.3	River, lake and tap water, dental waste water, chrome plating industry effluent, textile industry effluent	[83]
Pd	4-(2-benzothiazolylazo) 2,2′-biphenyldiol	CTAB	DMF	Spectrophotometry	0.6 ng mL^{-1}	2.0–240 ng mL^{-1}	50	Water, synthetic alloys, Pd-charcoal, plating effluents, catalyst and soil	[97]
Cu, Ni	BDAP	Triton X-114	1 mol L^{-1} HNO_3 in methanol (1:1)	FAAS	0.1 μg g^{-1} Cu 0.4 μg g^{-1} Ni	1.0–100.0 μg L^{-1} Cu 5.0–100.0 μg L^{-1} Ni	29 Cu, 25 Ni	Apple leaves, spinach leaves and tomato leaves	[98]
Cu	6-[20-(60-methyl-benzothiazolylazo)]-1,2-dihydroxy-3,5-benzenedisulfonic acid	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	1.5 μg L^{-1}	1.5–100 μg L^{-1}	14	River, waste, well and tap water	[99]
Pb, Cd	7-(6-methoxy-2-benzothiazolylazo)-8-hydroxyquinoline	Triton X-114	Ethanol	Spectrophotometry	3.9 ng mL^{-1} Pb 0.19 ng mL^{-1} Cd	5.00–100 ng mL^{-1} Pb 0.32–7.5 ng mL^{-1} Cd	114 Pb 84 Cd	Honey samples	[100]
Cd, Pb	TAC	Triton X-114	1% HNO_3 in ethanol	FAAS	0.077 μg L^{-1} Cd 1.05 μg L^{-1} Pb		22 Cd 56 Pb	Drinking water	[101]
V	TAC	Triton X-100	1 mol L^{-1} HNO_3 in methanol	GFAAS	0.05 ng mL^{-1}	1.0–60 ng mL^{-1}	10	Red and white wine, tea, and tomato	[102]
Ag	MBT	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	FAAS	2.2 ng mL^{-1}	10–200 ng mL^{-1}	46	Tap, spring, river distilled, water and photographic washing	[103]
Pt	MBT	Triton X-100	1 mol L^{-1} HCl	ICP-MS	0.4 μg kg^{-1}	0–10 μg L^{-1}		Coke and dust	[104]
Rh, Pd	MBT	Triton X-100	1 mol L^{-1} HCl	ICP-MS	1 ng L^{-1} Rh 5 ng L^{-1} Pd	0.0001–1 mg L^{-1}	8	Tablets	[105]
Pt					6 ng L^{-1} Pt				
Mn	Me-BTABr	Triton X-114	0.25–1 mol L^{-1} HNO_3	FAAS	0.7 μg L^{-1}	500–2500 μg L^{-1}	17	Shrimp powder, flaxseed flour, wheat flour, soy flour and oat, apple leaves and spinach leaves	[106]

Table 3 (*continued*)

Ion	Reagent	Micellar system	SRP diluting agent	Detection system	DL	Linearity	PF	Matrix	Ref.
Co, Ni	Me-BTABr	Tritorn X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	0.9 μg L^{-1} Co 1.1 μg L^{-1} Ni	0.9–100 μg L^{-1} Co 1.1–100 μg L^{-1} Ni	28 Co 23 Ni	Spinach leaves river, tap and well water	[107]
Cd	Br-TAO	Triton X-114	0.5 mol L^{-1} HCl	FAAS	0.5 μg L^{-1}	1.7–20 μg L^{-1}	27	Spinach leaves and tomato leaves	[108]
Mn	Br-TAO	Triton X-114	5.0×10^{-2} mol L^{-1} H_2SO_4	FAAS	0.5 μg L^{-1}	1.7–150 μg L^{-1}	14	Rice and corn flour, infant formula and tomato leaves	[109]
Cu	Sulfathiazolylazo resorsin	Triton X-100	0.1 mol L^{-1} HNO_3 in methanol	FAAS	0.64 μg L^{-1}	4–400 μg L^{-1}	25	Stream, waste, rain and tap water	[110]
Co	Br-TACl	Triton X-114	1 mol L^{-1} HNO_3 in ethanol	FAAS	2.8 μg L^{-1}	10–100 μg L^{-1}	25	Tablets: cyanocobalamin, hydroxycobalamin chloridrate, 5-deoxyadenosylcobalamin	[111]

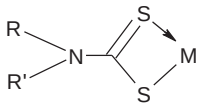


Fig. 7. Structure of dithiocarbamate complexes.

0.1 mol L^{-1} HCl. The diethyldithiocarbamates of Nb, Ru, Rh, Os, Ir and Pt are rarely poorly extractable [47].

In Table 4 we present some CPE methods proposed for metal preconcentration using dithiocarbamates as complexing compounds. As can be seen, dithiocarbamates are often used to study different kinds of speciation such as oxidation-state speciation of iron [113], chromium [133,136,138] and arsenic [122,134], fractionation of fulvic-bound and ionic copper in natural and waste water [129], tannin-bound and ionic iron in wine [128] or speciation analysis of inorganic mercury (Hg^{2+}) and methyl mercury ($MeHg^{+}$) in water and human hair samples [141].

It is worth mentioning the method for determination of inorganic Sb species by on-line cloud-point extraction combined with ETV-ICP-OES in different water and urine samples [118]. The method is based on the complexation of Sb(III) with APDC, which form a hydrophobic complex and subsequently enter surfactant-rich phase of Triton X-114 at pH 5.5, whereas Sb(V) remains in aqueous solutions. The micellar system containing the complex is then loaded into the FIA manifold, and the surfactant-rich phase retained in a microcolumn packed with absorbent cotton. After elution with acetonitrile, Sb(III) is determined by ETV-ICP-OES. Prior to determination of total Sb, Sb(V) is reduced to Sb(III) by L-cysteine. The content of Sb(V) is calculated by subtracting Sb(III) from total antimony. Under the optimized conditions the preconcentration factor achieved by the authors was 872 for Sb(III), and to the best of our knowledge it is the highest PF that has been obtained for the developed CPE preconcentration procedures for determination of metal ions.

4. Dithizone and its derivatives

Dithizone (diphenylthiocarbazone, H_2Dz) is one of the most well-known organic reagents used in analytical chemistry, including spectrophotometry for determination of metal ions, e.g. Pb, Zn, Cd, Ag, Pd, Hg, Cu and Bi, and for preconcentration of trace amounts of heavy metals prior to their determination.

Dithizone is practically insoluble in water at $pH < 7$ but it dissolves in alkaline aqueous media (> 20 g/L) forming orange-colored solutions containing the anionic form of HDz^{-}. Its solubility significantly increases in organic solvents such as ketones, alcohols, hydrocarbons, and chlorinated hydrocarbons, e.g. chloroform (1 g H_2Dz in 100 mL of CH_3Cl) and carbon tetrachloride (0.08 g H_2Dz in 100 mL of CCl_4). In organic solutions dithizone coexists in two tautomeric forms: ketone (I) and enol (II) (Fig. 8.) [47].

Dithizone reacts with most heavy metals whose sulfides are sparingly soluble in water. Metal ions react with dithizone forming nonpolar colored complexes whose colors differ significantly from dithizone. The exception is the palladium complex, which is gray-green. These nonpolar complexes are generally extracted into solvents like chloroform and carbon tetrachloride. This provides a convenient means of concentrating the complexes and increases analytical sensitivity.

It is a dibasic weak organic acid and depending on whether it reacts with the metal as a monobasic anion (HDz^{-}) or as a dibasic acid anion (Dz^{2-}), primary and secondary dithizonate complexes are formed, respectively. Most often, metals dithizonates are

Table 4
Dithiocarbamates used in CPE.

Ion	Reagent	Micellar system	SRP diluting agent	Detection system	DL	Linearity	PF	Matrix	Ref.
Fe	APDC total Fe ferrozine Fe(II)	Triton X-45 and Triton X-100 (6:4)	Methanol	Spectrophotometry FAAS	7 μg L^{-1} spectrophotometry, 3 μg L^{-1} FAAS	At levels near DLs up to 160 μg L^{-1} by spectrophotometry, at levels near DLs up to 100 μg L^{-1} by FAAS	50	River, ground, sea and tap water	[113]
Cd, Pb, Cr, Cu, Zn, Ni, Fe	APDC	Triton X-114	1 mol L^{-1} HNO_3 in methanol	ICP-OES, FAAS				Lake and river water	[114]
Cd, Pb, Cu, Cr, Zn, Fe	APDC	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS		0.02–4 μg L^{-1} Cd, 2.0–20 μg L^{-1} Pb, 1.0–30 μg L^{-1} Cr 0.5–30 μg L^{-1} Cu 10–100 μg L^{-1} Zn 10–100 μg L^{-1} or 100–400 μg L^{-1} Fe		River water	[115]
As	APDC	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	ETAAS	0.04 μg L^{-1}	0.1–20 μg L^{-1}	36	River and lake water	[116]
Co	APDC	Triton X-114	Ethanol	TS-FF-AAS	2.1 μg L^{-1}	0–0.1 mg L^{-1}		Cabbage, carrot, tomato leaves, beet, bovine liver, pig kidney, bovine rib, and bovine liver	[117]
Sb	APDC	Triton X-114	Acetonitrile	ETV-ICP-OES	0.09 μg L^{-1}		872	Pond, tap and river water, human urine	[118]
Cd	APDC	Triton X-114	10% HNO_3 in 20% methanol	TS-FF-AAS	0.04 μg L^{-1}	0.1–5 μg L^{-1}	13	River water, urine	[119]
Ag, Co, Cr, Cu, Fe, Mn, Ni, Pb	APDC	Triton X-114	0.2 mol L^{-1} HNO_3 in methanol	ETAAS	0.003 ng mL^{-1} Ag 0.008 ng mL^{-1} Co 0.003 ng mL^{-1} Cr 0.006 ng mL^{-1} Cu 0.015 ng mL^{-1} Fe 0.002 ng mL^{-1} Mn 0.009 ng mL^{-1} Ni 0.01 ng mL^{-1} Pb	0.02–0.16 ng mL^{-1} Ag 0.0–0.50 ng mL^{-1} Co 0.01–0.10 ng mL^{-1} Cr 0.04–1.30 ng mL^{-1} Cu 0.06–0.70 ng mL^{-1} Fe 0.01–0.30 ng mL^{-1} Mn 0.03–0.90 ng mL^{-1} Ni 0.04–1.30 ng mL^{-1} Pb	200	Near shore seawater, seawater and natural water	[120]
Sb	APDC	Triton X-114	0.2 mol L^{-1} HNO_3 in methanol	ETAAS	0.03 μg L^{-1}	0.1–3.5 μg L^{-1}	28	Lake and well water	[121]
As	APDC	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	ETAAS	0.02 μg L^{-1} total As 0.03 μg L^{-1} As(III)	0.5–20 μg L^{-1} total As 0.2–20 μg L^{-1} As(III)	40	Canal, hand pump and tube well water	[122]
As	APDC	Triton X-114	0.1 mol L^{-1} HNO_3 in ethanol	ETAAS	0.025 ng g^{-1}	0.2–20 μg L^{-1}	50	Maize (grains, shoots and roots) and soil	[123]
Sb	APDC	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	ETAAS	0.02 ng mL^{-1}	0.1–3 ng mL^{-1}		Food packaging materials: ceramic container, plastic drinking cups, plastic drinking-water pipes	[124]
As	APDC	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	ETAAS	0.025 μg kg^{-1}	1–10 μg L^{-1}	20	Human hair	[125]
Cr	APDC	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	0.6 μg L^{-1}	Up to 100 μg L^{-1}		Sea, river and lake water, urine	[126]

Table 4 (*continued*)

Ion	Reagent	Micellar system	SRP diluting agent	Detection system	DL	Linearity	PF	Matrix	Ref.
Fe, Co, Ni	APDC	Triton X-114	Methanolic solution of 70 g L^{-1} HCl containing 1 g L^{-1} KCl and 50 g L^{-1} 8-HQ	FAAS	19 μg L^{-1} Fe 5 μg L^{-1} Co 11 μg L^{-1} Ni	Up to 350 μg L^{-1} Fe Up to 200 μg L^{-1} Co Up to 250 μg L^{-1} Ni	20	Sea, river, tap and waste water, red wine, settled sewage	[127]
Fe	Bond with tannins and other related compounds - non chelating agent Free-APDC	Triton X-45 and Triton X-100 (6:4)	Methanolic solution of 70 g L^{-1} HCl containing 1 g L^{-1} KCl and 50 g L^{-1} 8-HQ	FAAS	20 μg L^{-1}	At levels near DLs up to 350 μg L^{-1}		Wine	[128]
Cu	Labile APDC	Triton X-100 and Triton X-45	1 mol L^{-1} HNO_3 in methanol	FAAS	8.5 μg L^{-1} bound species	40–150 μg L^{-1} bound species	50 Bound	Raw sewage, Settled sewage, river water	[129]
	Bond none	CTAB and TX100/45			0.9 μg L^{-1} labile species	4–40 μg L^{-1} labile species	100 Labile		
Pb	APDC	Triton X-114	Acetonitrile	ETAAS	44.6 ng L^{-1}	0.2–4 μg L^{-1}	22.5	Prawn, tea, rice, peach leaves	[130]
Cd, Sb, Hg	APDC	Triton X-114	1% NHO_3	Flow injection vapor generation inductively coupled plasma mass Spectrometry (FI-VG-ICP-MS)	0.002 ng mL^{-1} Cd 0.0006 ng mL^{-1} Sb 0.005 ng mL^{-1} Hg	0.05–2 ng mL^{-1}		River, estuarine, bottled mineral, reservoir and tap water	[131]
Pd, Pt, Au	APDC	Tergitol TMN-6		FAAS	1.4 ng mL^{-1} Pd 2.8 ng mL^{-1} Pt 1.2 ng mL^{-1} Au		21 Pd 12 Pt 24 Au	Soil of industrial sewage samples	[132]
Cr	None Cr(VI)	Triton X-114 and Aliquat-336	0.2% HCl	ICP-DRC-MS	0.010 ng mL^{-1} Cr(VI)	0.2–10 ng mL^{-1} Cr(VI)	10	Tap, lake, underground, municipal water	[133]
	APDC Cr(III)				0.025 ng mL^{-1} Cr(III)	0.3–5 ng mL^{-1} Cr(III)			
As	APDC As(III) Molybdate As(V)	Triton X-114	HNO_3 in methanol (1:10)	ETAAS	0.04 μg L^{-1} As(III) 0.20 μg L^{-1} As(V)	At levels near QLs up to 20 μg L^{-1}		Ground water	[134]
Pb	APDC, DDTC	Triton X-114	0.1 mol L^{-1} HNO_3 in ethanol	FAAS	1.14 μg L^{-1}	5–20 μg L^{-1}	56 APDC 42 DDTC	Human blood	[135]
Cr	APDC Cr(VI) 8-HQ Cr(III)	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	1.4 μg L^{-1}Cr(III) 0.65 μg L^{-1} Cr(VI)	Up to 130 μg L^{-1} Cr(III) Up to 85 μg L^{-1} Cr(VI)	75 Cr(III) 120 Cr(VI)	Sea and river water, tobacco	[136]
Cu	DDTC	Triton X-114 and octanol	Ethanol	Spectrophotometry	7 μg L^{-1} without RS-CPE, 0.4 μg L^{-1} with RS-CPE	At levels near DLs up to 5000 μg L^{-1} without RS-CPE, at levels near DLs up to 50 μg L^{-1} with RS-CPE	18	Defatted milk powder, tea, tap and lake water	[137]
Cr	DDTC	Triton X-114	Methanol	HPLC with UV detection	3.4 μg L^{-1} Cr(III) 5.2 μg L^{-1} Cr(VI)	50–1000 μg L^{-1} Cr(III) 50–2000 μg L^{-1} Cr(VI)	65 Cr(III) 19 Cr(VI)	Snow, river, sea and waste water	[138]
Hg	DDTC	Triton X-100		Spectrophotometry	0.53 μg L^{-1}	4–240 μg L^{-1}			[139]
Se, Sb	DDTC	Triton X-114	Ethanol	ETV-ICP-MS	0.05 μg L^{-1}Se 0.03 μg L^{-1} Sb	0.25–50 μg L^{-1}	50	Pool, lake, river and tap water	[140]
Hg	DDTC	Triton X-114	Methanol	HPLC combined with ICP-MS	4 ng L^{-1} Hg 10 ng L^{-1} $MeHg^+$	0.05–10 μg L^{-1}	42 Hg 21 $MeHg^+$	Tap and river water, human hair	[141]
Pt	DDTC	Triton X-114	0.1 mol L^{-1} HNO_3 in water–methanol mixture (80/20, v/v)	GFAAS	0.2 ng mL^{-1}	0.7–15 ng mL^{-1}	29	Stainless steel surfaces inside isolators, floors, drug vials, drug storage boxes, transport boxes, gloves (nitrile, vinyl, latex and neoprene) and infusion bags	[142]
Cu, Ag	DDTC	Triton X-114	10% HNO_3 in 20% methanol	FAAS	0.5 μg L^{-1} Cu 1 μg L^{-1} Ag	5–300 μg L^{-1} Cu 5–450 μg L^{-1} Ag	22 Cu 24 Ag		[143]

							artificial seawater, reagents:$Zn(NO_3)_2$, $Co(NO_3)_2$, $CdCl_2$	
Cr	DDTC	Triton X-100	1 mol L^{-1} HNO_3 in methanol	FAAS	0.08 μg L^{-1}	Up to 100 μg L^{-1}	98	Tap, well, dam, industrial waste water	[144]
Ag	DDTC	Triton X-114	10% HNO3 in 20% methanol	TS-FF-AAS	0.2 μg L^{-1}	Up to 20 μg L^{-1}	21	Soil, marine sediment, silver ore	[145]
Ni, Cd, Pb, Cu	DDTC	Triton X-114	1% HNO_3 in methanol	ICP-OES	0.030 μg L^{-1} Cd 2.1 μg L^{-1} Pb 0.62 μg L^{-1} Cu 0.27 μg L^{-1} Ni	0–12 μg L^{-1} Cd 0–50 μg L^{-1} Pb 0–25 μg L^{-1} Cu 0–25 μg L^{-1} Ni	20 Cd 20.4 Pb 19.5 Cu 20.6 Ni	Sea water, petroleum formation produced water	[146]
Cu	DDTC	Triton X-100	10% HNO_3 in 20% methanol	TS-FF-AAS	0.2 μg L^{-1}	Up to 80 μg L^{-1}	114	Tap, lake and river water, milk powder and tea	[147]
Ni	DDTC	Triton X-100	Ethanol	Spectrophotometry	0.5 ng mL^{-1}	2–100 ng mL^{-1}	72	Soil, stream sediments, water	[148]

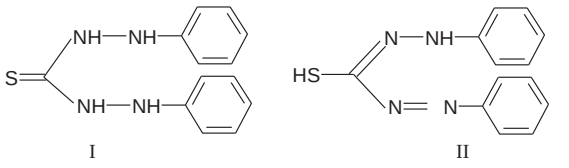


Fig. 8. Structure of two tautomeric forms of dithizone: ketone (I) and enol (II).

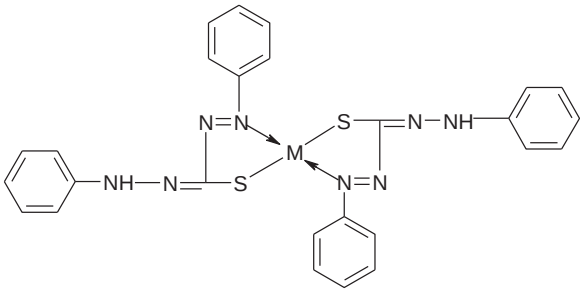


Fig. 9. Structure of the primary dithizonate complexes.

formed by the reaction

$$M^{n+} + nH_2Dz \rightleftarrows M(HDz)_n + nH^+$$

Only certain metals such as Cu, Hg, Ag, Pt, Au, and Pd form secondary dithizonates when dithizone reacts with a metal as the anion of a dibasic acid (Dz^{2-}), e.g. CuDz and Ag_2Dz [149]. In general, an acidic environment and large excess of dithizone favors formation of primary dithizonates, and alkaline environment and insufficiency of the reagent favor formation of secondary dithizonates, according to the reaction

$$2M(HDz)_n \rightleftarrows M_2Dz_n + nH_2Dz$$

Studies on the structure of primary dithizonates showed that the metal binds to sulfur atoms, replacing thiol group hydrogen; the metal also binds coordinatively through nitrogen atoms (Fig. 9).

The most stable dithizonates (those of Pt, Pd, Au, Ag, Hg and Cu) can be extracted from strongly acid solutions. Some metals such as Bi, In and Zn are extractable from weakly acid media, whereas other metals (Co, Ni, Pb, Tl, and Cd) are extractable from neutral or alkaline media. The higher the excess of dithizone, the lower the pH at which the dithizonate forms. The pH at which extraction of individual metal starts is approximately 1.5 pH units higher with dithizone in chloroform than with dithizone in carbon tetrachloride. Irrespective of their thermodynamic stability, the dithizonates of certain metals, e.g. Ag, Hg, Pb and Cd are extracted rapidly whereas those of other metals (Pd, Cu, and Zn) require prolonged shaking with the organic solution of dithizone. This is explicable in terms of the kinetics of dithizonate formation. The extractability of dithizonate complexes with metals decreases in the following order: Pd, Ag, Hg(II), Cu(II), Bi, Pt(II), Tl(III), Fe(II), Sn(II), Co, Ni, Zn, Pb, Mn, Cd [47,150].

The selectivity of methods for preconcentration and determination of metals using dithizone can be achieved by controlling the acidity of the medium and using masking agents such as cyanide, EDTA, thiosulphate and iodide.

In Table 5 we show CPE methods based on complexes with dithizone and its derivatives developed for trace metal analysis. Compared to the previously discussed groups of ligands, only a few procedures were developed using dithizone, may be due to the fact that even a commercial product must almost always be purified before use due to oxidation of the reagent. Moreover, the purification process is time-consuming and requires the usage of large volumes of chloroform which is unfriendly both to the environment and to humans. Nevertheless, among the analytical

Table 5
Dithizone and its derivatives used in CPE.

Ion	Reagent	Micellar system	SRP diluting agent	Detection system	DL	Linearity	PF	Matrix	Ref.
Pb	Dithizone	Triton X-114 and octanol	1 mol L^{-1} HNO_3 in methanol	FAAS	310 μg L^{-1} without RS-CPE, 4.3 μg L^{-1} with RS-CPE	At levels near DLs up to 40 mg L^{-1} without RS-CPE, At levels near DLs up to 1.2 mg L^{-1} with RS-CPE	39	Tap, river and lake water	[151]
Ag	Dithizone	Triton X-114	THF	FAAS	0.56 ng mL^{-1}	3–200 ng mL^{-1}	43	Waste, river, sea, tap and rain water	[152]
Hg	Dithizone	Triton X-100	Water	Spectrophotometry	0.014 μg L^{-1}	0.05–0.5 μg L^{-1}	6	Natural water	[153]
Cd, Ni	Dithizone	Triton X-114	THF	FAAS	0.31 ng mL^{-1} Cd 1.2 ng mL^{-1} Ni	1–100 ng mL^{-1} Cd 4–180 ng mL^{-1}	52 Cd 39 Ni	Waste, tap, river and sea water	[154]
Bi	Dithizone	Triton X-114	THF	ETAAS	0.02 ng mL^{-1}	0.04–0.60 ng mL^{-1}	196	Tap water, urine and hair	[155]
Cd, Co, Cr, Mn	Dithizone	Triton X-114	HNO_3 (1:1)	ICP-OES	0.093 μg L^{-1} Cd 0.20 μg L^{-1} Co 0.73 μg L^{-1} Cr 1.2 μg L^{-1} Mn	5–80 μg L^{-1}	21 Cd 21 Co 9 Cr 19 Mn	Petroleum produced water	[156]
Cd	Dithizone	Triton X-114	THF	ETVAFS, ETAAS	0.01 μg L^{-1} ETVAFS 0.03 μg L^{-1} ETAAS	Up to 0.5 μg L^{-1} ETVAFS Up to 2 μg L^{-1} ETAAS	152 ETV-AFS 93 ET-AAS	Rice and water	[157]
Hg	Dithizone	Triton X-114	4 mol L^{-1} HNO_3	CVAFS	5 pg mL^{-1}	0.05–5 ng mL^{-1}	29	Tap, river, lake and waste water	[158]
Ag	Dithizone	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	1.42 ng mL^{-1}	5–50 ng mL^{-1}	37	Spiked/fortified water, dogfish muscle and liver	[159]
Ag	Dithizone	Triton X-114	THF	FAAS	0.7 μg L^{-1}	4–220 μg L^{-1}	38	Tap, rain, river, sea and deionized water	[160]
Bi	Dithizone	Triton X-100	1 mol L^{-1} HNO_3 in methanol	FAAS	4.0 μg L^{-1}		43	Water and geological samples	[161]
Cu	4-ethyl-1-(pyridin-2-yl)thiosemicarbazide	Triton X-114	Methanol	Spectrophotometry	0.1 ng mL^{-1}	0.1–25 ng mL^{-1}		Distilled, tap, river and lake water; saline solutions of: $MgSO_4$, K_2SO_4, Na_2SO_4, Na_2HPO_4, NaCl, KCl	[162]
Pt	4-(p-chlorophenyl)-1-(pyridin-2-yl)thiosemicarbazide	Triton X-114	Mixture of metanol and HNO_3 (5:1)	GFAAS	0.25 ng mL^{-1}	up to 50 ng mL^{-1}	47	Tap, river, brackish, sea and industrial waste water, road dust and rock, rice, flour, beans	[163]
Pb, Co, Cu	1-Phenylthiosemi-carbazide	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	3.42 μg L^{-1} Pb 1.00 μg L^{-1} Co 0.67 μg L^{-1} Cu	0.25–5 mg L^{-1} Co 0.5–10 mg L^{-1} Pb 0.25–5 mg L^{-1}Cu	25	Tap, spring and sea water, canned fish, black and green tea, tomato sauce and honey	[164]
Cr	1,5-Diphenylcarbazide	Triton X-114 and SDS	0.1 mol L^{-1} HNO_3 in ethanol	ETAAS	1 ng L^{-1}	3–300 ng L^{-1}	92	Tap and river water	[165]

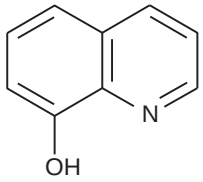


Fig. 10. Structure of 8-hydroxyquinoline.

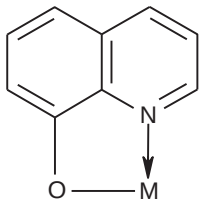


Fig. 11. Structure of oxinate complexes.

procedures presented in Table 5, noteworthy is the method for speciation analysis of chromium in water samples by electrothermal atomic absorption spectrometry (ET-AAS) proposed by Ezoddin et al. [165]. The method is based on the reaction of Cr(VI) with 1,5-diphenylecarbazide (DPC) in an HCl medium and the formation of Cr(III) diphenylcarbazone complex. This cationic complex was selectively extracted into anionic mixed micelle comprising sodium dodecyl sulfate (SDS) and Triton X-114. Total chromium was subjected to similar extraction procedure after oxidation. The Cr(III) content was calculated by subtracting Cr(VI) from the total chromium. Under optimum conditions, a detection limit of 1 ng L^{-1} with preconcentration factor of 92 was achieved which is comparable or superior to other CPE procedures for chromium determination. The study by Ezoddin et al. indicates that preconcentration of hydrophilic water-soluble metal ions is also feasible using CPE technique. Moreover, these authors demonstrated high reactivity of the hydrophobic solubilizing sites of mixed micelles which makes extraction of complexes temperature-independend. From a practical point of view, due to room temperature phase separation and stability of the extracted chromium species in a surfactant-rich phase, the proposed methodology may be useful to handle samples at sampling sites and transport small volumes of surfactant-rich phases containing Cr species to environmental laboratories for further analysis.

5. 8-Hydroxyquinoline and its derivatives

8-Hydroxyquinoline (oxine, 8-HQ) is one of the most popular and versatile reagents widely utilized in analytical chemistry. 8-HQ is amphoteric in aqueous solutions due to the presence of basic nitrogen and phenolic hydroxyl group in the molecule (Fig. 10).

8-HQ dissolves in alkaline solutions as the oxinate ion and in acid solutions as the oxinum cation. The oxine is also readily soluble in chloroform (3.938 g 8-HQ in 10 mL of CH_3Cl), carbon tetrachloride (1.278 g 8-HQ in 10 mL of CCl_4), benzene (2.227 g 8-HQ in 10 mL of C_6H_6), ethanol, acetone and other organic solvents. The distribution of 8-hydroxyquinoline between the organic phase and water depends largely on the pH of the solution [47,150].

8-HQ reacts with at least 43 metals, giving sparingly soluble deposits. These compounds are inner-complex salts of 5-membered rings (Fig. 11). In general, it reacts with the same metals that are precipitated with ammonia solution. The general formula of chelated di- and trivalent metal is: $M(C_9H_6ON)_2$ or $M(C_9H_6ON)_3$. The composition of metal complexes at higher oxidation states may be partially different, e.g. $Ce(C_9H_6ON)_4$, $MoO_2(C_9H_6ON)_2$ or $Th(C_9H_6ON)_4(C_9H_7ON)$. Oxime complexes form in a wide pH range (from 2 to nearly 14), but the optimal pH of the complexation reaction strongly depends on solution ionic strength, temperature, type of metal and its concentration, and reagent excess. Moreover, the weaker the oxinate complex formed, the more alkaline the pH range of the complexation reaction. It is also important to know that oxine reacts with elements at a certain state of oxidation (e.g. Fe (III), and Cr (III)), which is related to its reducing or oxidizing properties. And so, before chromate (VI) ions form a complex with oxine, they are reduced to Cr (III). This property of 8-HQ can be used to study speciation of chromium in various water samples [136]. Moreover, some oxinate complexes are fluorescent and this property was applied in the spectrofluorimetric determination of Al [168–170,174], Zn [168], Cr [166] and V [177]. In Table 6 we summarized CPE methods for metal determination based on oxine and its derivatives. As can be seen, 8-hydroxyquinoline can be used both for selective and group preconcentration and it allows achieving high preconcentration factors of up to 200 [174].

6. Ammonium O,O′-diethyldithiophosphate (DDTP) in CPE

The ammonium salt of O,O-diethyl-dithiophosphoric acid (DDTP) was first studied in the 1960s by Bode and Arnswald [185,186], who showed that it does not react with alkaline, alkaline earth elements and others, such as Mn, V, Ti, Co, Cr, Zn, etc., being quite selective. More recently, other authors employed DDTP in separation processes, including CPE due to its sufficient hydrophobicity. DDTP, which has a sulfur atom as the electron donor, behaves like a soft base, and can complex elements that are mildly acidic. This agent is advantageous because it forms quite stable chelates, even in acidic medium, that result from sample dissolving procedures. Hence, the use of buffers, which are sources of contamination, is not required. Therefore, it is used in the preconcentration of heavy metals in different materials such as water and biological materials. In Table 7 we present CPE methods based on DDTP complexes with metal ions.

7. Schiff bases used in CPE

Schiff-bases are considered a very important class of organic compounds, having wide occurrence in many aspects of biology (proteins, visual pigments, enzymic aldolization and decarboxylation reactions). Moreover, some Schiff bases and their metal complexes exhibit biological activity and behave like antibiotic, antiviral or antitumor agents. They are also used as catalysts in polymer and dye industries, and find application as antifertility and enzymatic agents. An interesting application of Schiff bases is their use as an effective corrosion inhibitor. It is based on their ability to spontaneously form a monolayer on the surface to be protected [199–201].

In analytical chemistry, Schiff bases are used e.g. in optical and electrochemical sensors, as well as in various chromatographic methods, to enable detection of enhanced selectivity and sensitivity. Moreover, Schiff bases are applicable in analytical determination, using reactions of condensation of primary amines and carbonyl compounds in which the azomethine bond is formed (determination of compounds with an amino or carbonyl group); using complex formation reactions (determination of amines, carbonyl compounds and metal ions); or utilizing the variation

Table 6
8-Hydroxyquinoline and its derivatives used in CPE.

Ion	Reagent	Micellar system	SRP diluting agent	Detection system	DL	Linearity	PF	Matrix	Ref.
Cr	8-HQ	Triton X-114	Methanol	SPF	0.2 μg L^{-1}	0.5–10 μg	75	River and sea water, tablets Centrum	[166]
Sn	8-HQ	Triton X-114	1% HNO_3 in methanol	GFAAS	0.012 ng mL^{-1}	0.05–2.0 ng mL^{-1}	96.2	Tap, sea and river water	[167]
Al, Zn	8-HQ	Triton X-114	Ethanol	SPF	0.79 μg Al 1.2 μg Zn	2–200 μg Al 5–250 μg Zn	10	Mineral and tap water, apple, tomato, carrot, potato, yoghurt, bread, wheat flour, sausage	[168]
Al	8-HQ	Triton X-114	Water–ethanol (1:1) mixture for SPF 0.1 mol L^{-1} HNO_3 in ethanol for FAAS	SPF FAAS	0.25 μg	5–50 μg	100	Mineral water, parenteral solutions, pharmaceutical formulations: sodium bicarbonate, sodium heparin, vitamin solution, human albumin, amino acid 10%	[169]
Al	8-HQ	Triton X-114	Water–ethanol (1:1) mixture for SPF 0.1 mol L^{-1} HNO_3 in ethanol for FAAS	SPF FAAS	0.5 μg	10–200 μg	20	Lake, river and canal water	[170]
V	8-HQ	Triton X-114	HNO_3 in ethanol (1:10)	ETAAS	42 ng L^{-1}	2–50 μg	125	Parenteral solutions, pharmaceutical formulations: sodium bicarbonate, sodium heparin, vitamin solution, human albumin, amino acid 10%	[171]
Ce, Er, Gd,Nd, Pr, Sm, Tb,Tm, Dy,Eu, Ho, La, Lu, Sc, Y, Yb	8-HQ	Triton X-114	0.5 mol L^{-1} HCl	ICP-OES	41.4 pg mL^{-1} (Yb) to 448 pg mL^{-1} (Gd) with chelating agent 69.0 pg mL^{-1} (Sc) to 509.5 pg mL^{-1} (Sm) without chelating agent	2–1000 ng mL^{-1} Dy, Eu, Ho, La, Lu, Sc, Y, Yb 5–1000 ng mL^{-1} Ce, Er, Gd, Nd, Pr, Sm, Tb, Tm.		Pork liver, *Auricularia auricula*, mushroom and tea leaves,	[172]
Bi	8-HQ	Triton X-114	0.1 mol L^{-1} HNO_3 in ethanol	ICP-OES	0.12 ng mL^{-1}	Up to 50 ng mL^{-1}	81	Human serum	[173]
Al	8-HQ	Triton X-114	Water–ethanol-mixture for SPF 0.1 mol L^{-1} HNO_3 in ethanol for FAAS	SPF FAAS	0.384 μg	10–50 μg	200	Dialysate samples	[174]
Mo	8-HQ	Triton X-100	Water	ID-ICP-MS	0.8 ng g^{-1}		70	Peach leaves, apple leaves, rice flour, rye grass, wheat flour	[175]
Cr	8-HQ	Triton X-100	0.1 mol L^{-1} HNO_3	GFAAS	0.022 μg	0.5–10 μg	50	Cigarettes and cigarette ashes	[176]
V	8-HQ	Triton X-114	Formic acid	SPF	0.007 μg	0.02–10 μg	50	Tap water, hair, tablets	[177]
Cu, Cr, Fe, Mn, Pb, Cd, Co, Ni, Zn	8-HQ	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	25 ng L^{-1} Cu 75 ng L^{-1} Cr 105 ng L^{-1} Fe 33 ng L^{-1} Mn 167 ng L^{-1} Pb 16 ng L^{-1} Cd 4.5 ng L^{-1} Co 130 ng L^{-1} Ni 35 ng L^{-1} Zn	2.5–4500 μg L^{-1}	100	Lake, waste and distilled water	[178]

Cd, Co, Ni, Pb, Zn, Cu	8-HQ	Triton X-114		ICP-OES	0.01 μg for Cd, 0.04 μg for Co, 0.01 μg for Ni, 0.34 μg for Pb, 0.05 μg for Zn, 0.04 μg for Cu	0.08–0.4 μg mL^{-1} Cd 0.08–0.32 μg mL^{-1} Co 0.08–0.4 μg mL^{-1} Ni 0.04–0.28 μg mL^{-1} Pb 0.04–0.4 μg mL^{-1} Zn 0.04–0.4 μg mL^{-1} Cu	19.72 Cd 9.95 Co 19.97 Ni 10.54 Pb 18.85 Zn 22.16 Cu	River water	[179]
Co, Pb	8-HQ	Triton X-114	0.1 mol L^{-1} HNO_3 in ethanol	FAAS	0.26 μg L^{-1} Co 0.44 μgL^{-1} Ni	5–20 μg	70 Co 50 Pb	Canal and waste water,	[180]
U	8-HQ	Triton X-114		ICP-OES					[181]
Mn	8-HQ	Triton X-100	0.1 mol L^{-1} HNO_3 in methanol	FAAS	1.9 μg L^{-1}	6.5–265 μg L^{-1}	10	Tea samples, tap, lake and artificial sea water, mussel tissue	[182]
Fe,	2-methyl-8-quinolinol	Triton X-100	0.1 mol L^{-1} HCl	GFAAS				River water	[183]
Pb, Cd	7-(6-methoxy-2-benzothiazolylazo)-8-hydroxyquinoline	Triton X-114	Ethanol	Spectrophotometry	3.9 ng mL^{-1} Pb 0.19 ng mL^{-1} Cd	5.00–100 ng mL^{-1} Pb 0.32–7.5 ng mL^{-1} Cd	114 Pb 84 Cd	Honey samples	[100]
Zn	2-methyl-8-hydroxyquinoline PAN	Triton X-114	0.1 mol L^{-1} HNO_3 in ethanol	FAAS	1.4 μg 1.52 μg PAN	5–20 μg	30 26 PAN	Medicinal plants. human blood	[78]
Cr	APDC Cr(VI) 8-hydroxyquinoline Cr(III)	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	1.4 μg Cr(III) 0.65 μg Cr(VI)	Up to 130 μg Cr(III) Up to 85 μg Cr(VI)	75 Cr(III) 120 Cr(VI)	Sea and river water, tobacco	[136]
Fe	8-hydroxy-7-iodoquinoline-5-sulfonic acid	Triton X-114	Ethanol	FAAS	1.7 μg	20–250 or 5–150 μg	75 or 149	Infant dry formula milk, human and cow's milk, tap, river, spring and rain water	[184]

Table 7
Application of ammonium O,O′-diethyldithiophosphate (DDTP) in CPE preconcentration of metals.

Ion	Micellar system	SRP diluting agent	Detection system	DL	Linearity	PF	Matrix	Ref.
Ag, As, Au, Cd, Cu, Pb, Se	Triton X-114	1% HNO_3 in methanol	ICP-MS	0.03 μg L^{-1} Cu 0.006 μg L^{-1} As 0.02 μg L^{-1} Se 0.004 μg L^{-1} Ag 0.006 μg L^{-1} Cd 0.003 μg L^{-1} Au 0.004 μg L^{-1} Pb	0.1–1 μg L^{-1} Cu and As, 0.01–0.5 μg L^{-1} Ag, Au, Cd, Pb, Se	17 Cu 42 As 37 Se 20 Ag 29 Cd 30 Au 25 Pb	River, sea and enriched water	[187]
Ru, Rh, Pd, Pt, Au	Triton X-114	0.125 mol L^{-1} HCl in 60% methanol	ETV-ICP-MS	0.7 ng L^{-1} Ru 3 ng L^{-1} Rh 6 ng L^{-1} Pd 0.6 ng L^{-1} Pt 0.8 ng L^{-1} Au		44 Ru 7 Rh 40 Pd 60 Pt 35 Au	Human hair and human urine	[188]
Cu	Triton X-100	0.1 mol L^{-1} HNO_3 in methanol	FAAS	0.94 ng mL^{-1}	5–200 ng mL^{-1}		Drinking and rain water, serum and human hair	[189]
Cd	Triton X-114	0.1 mol L^{-1} HNO_3 in ethanol	FAAS	0.9 μg L^{-1}	3–400 μg L^{-1}		Mineral and lake water, physiological solution, tobacco	[190]
Cd, Pb	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	ETAAS	6 ng g^{-1} Cd 40 ng g^{-1} Pb		129 Cd 18 Pb	Mussel tissue, human hair, bovine muscle, pig kidney	[191]
Hg	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	CVAAS	0.4 ng g^{-1}	1–12 μg L^{-1}	10	Human hair, dogfish Liver, dogfish muscle	[192]
Pb, Cd	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	GFAAS	40 ng L^{-1} Pb 2 ng L^{-1} Cd		16	Urine	[193]
Hg	Triton X-114	0.1 mol L^{-1} HCl in methanol	CVAAS	0.117 μg kg^{-1}	At levels near DLs up to 10 μg L^{-1}	12	Broiler chicken tissues (leg, breast, liver and heart)	[194]
Hg	Triton X-114	0.5 mol L^{-1} HCl	CV-ICP-OES	2.2 ng g^{-1} 0.044 μg L^{-1}		13	Honey	[195]
Cd, Pb, Pd	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	ETAAS	0.02 μg L^{-1} Cd 0.08 μg L^{-1} Pb 0.014 μg L^{-1} Pd	0.05–0.5 μg L^{-1} Cd 0.2–2.5 μg L^{-1} Pb 0.1–2 μg L^{-1} Pd	71 Cd 34 Pb 100 Pd	Human blood	[196]
As, Bi, Cd, Pb	Triton X-114	Methanol with addition of 0.6 mol L^{-1} HCl As, 0.7 mol L^{-1} HNO3 or 0.5 mol L^{-1} HCl for Bi, 0.70 mol L^{-1} HNO3 Cd and Pb	ICP-OES	0.055 μg L^{-1} As 0.063 μg L^{-1} Bi 0.047 μg L^{-1} Cd 0.28 μg L^{-1} Pb	0.5–10 μg L^{-1} As, Bi 1–15 μg L^{-1} Cd 5–25 μg L^{-1} Pb	10 As 18 Bi 12 Cd 14 Pb	Enriched water, oyster tissue, tobacco leaves, bush branches and leaves; river water, wine, fertilizer, urine	[197]
Sb	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	GFAAS	0.08 μg L^{-1}	0.25–16 μg L^{-1}	229	River, sea, mineral and stream water, blood serum	[198]

Table 8
Schiff bases used for CPE preconcentration of metal ions.

Ion	Reagent	Micellar system	SRP diluting agent	Detection system	DL	Linearity	PF	Matrix	Ref.
Ag	Bis(2-mercaptoanil) acetylacetone	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	FAAS	0.43 ng mL^{-1}	2–200 ng mL^{-1}	50	Sea, river, waste, mineral, tap and rain water	[207]
Cd	Glyoxal-bis (2-hydroxyanil)	Triton X-114 and SDS	Ethanol	ETAAS	7 ng L^{-1}	0.02–0.4 μg L^{-1}	22	Tap, lake, sea water, tabacco, geological sample IAEA-405	[208]
Ag, Zn, Pb	2-(((1*H*-benzo[*d*]imidazol-2-yl)methoxy)methyl)-1*H*-benzo[*d*]imidazole	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	2.8 ng mL^{-1} Pb 1.7 ng mL^{-1} Ag 1.1 ng mL^{-1} Zn	8–900 ng mL^{-1} Pb 0.9–900 ng mL^{-1} Ag 0.8–800 ng mL^{-1} Zn	30	Radiology waste water, amalgam alloy, blood and lotus (tree)	[209]
Ag	Bis((1*H*-benzo[*d*]imidazol-2yl)methyl)sulfane	Triton X-114	2 mol L^{-1} HNO_3 in methanol	FAAS	1.9 ng L^{-1}	2–400 ng L^{-1}	39	Tap, river and waste water and blood	[210]
Cd, Pb, Pd, Ag	Bis((1H-benzo [d] imidazol-2yl)ethyl) sulfane	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	1.4 ng mL^{-1} Cd 2.8 ng mL^{-1} Pb 1.6 ng mL^{-1} Pd 1.4 ng mL^{-1} Ag		30	Radiology waste, vegetable, blood and urine	[211]
Cd, Cu, Co, Ni	*N*,*N*′-bis[(1*R*)-1-ethyl-2-hydroxyethyl]ethanediamide-DAD1 *N*,*N*′-bis[(1*S*)-1-benzyl-2-hydroxyethyl]-ethanediamide-DAD2	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	0.45 ng mL^{-1} Cd, 0.50 ng mL^{-1} Cu, 1.25 ng mL^{-1} Co, 0.60 ng mL^{-1} Ni	2.5–25.0 ng mL^{-1} Cu and Cd, 5.0–25 ng L^{-1} Co and Ni	For DAD1 18 Cd, 23 Cu, 18 Co, 20 Ni For DAD2 20 Cd, 22 Cu, 17 Co, 20 Ni	Tap and waste water	[212]
Fe	N,N′-(2,2′-(ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(2-chloroacetamide)	Triton X-114	Conc. HNO_3	FAAS	1.22 μg L^{-1}	0.2–5 mg L^{-1}	10	Sea, stream and tap water, soil, tobacco, black tea	[213]
Cr	(bis(2-methoxybenzaldehyde) ethylene diamine	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	0.17 μg L^{-1}	0.17–150 μg L^{-1}	57	Tap and river water	[214]
Cu	N,N′-bis(2-hydroxyacetophenone)-1,2-propanediimine	Triton X-114	0.5 mol L^{-1} HNO_3 in methanol	FAAS	0.03 ng mL^{-1}	0.1–1300 ng L^{-1}	20	Tap, well, river and rain water	[215]
Cd	L22pysa ($C_{24}H_{26}N_4O_2$)	Triton X-114	0.5 mol L^{-1} HNO_3 in methanol	FAAS	0.44 ng L^{-1}	1–100 ng L^{-1}	20	Rice, snow, river, rain, tap and mineral water	[216]
Ni	N,N′-bis(salicylidene)-1,2-ethanediamine	Tergitol TMN-6		FAAS	1 μg L^{-1}	10–500 μg L^{-1}	30	Water samples	[217]
Pd, Pb	Dimethylglyoxime	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	1 ng mL^{-1} Pd 1.4 ng mL^{-1} Pb		51 Pd 44 Pb	Street dust, soil, radiology waste, catalytic converter, and urban aerosol samples	[218]
Ag, Pd	2-((2-((1H-benzo[d]imidazole-2-yl)methoxy)phenoxy)-metyl)-1H-benzo[metyl]imidazol	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	10 μg L^{-1} Ag 25 μg L^{-1} Pd	28–430 μg L^{-1} Ag 57–720 μg L^{-1} Pd	35 Ag 28 Pd	Waste water, soil, hydrogenation catalyst samples	[219]
Cu	2-[(2-mercaptophenylimino)-methyl]phenol	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	0.15 μg L^{-1}	1–150 μg L^{-1}	81	Rice flour, sea and river water	[220]

Table 8 (*continued*)

Ion	Reagent	Micellar system	SRP diluting agent	Detection system	DL	Linearity	PF	Matrix	Ref.
Mg, Ag	4 methyl-3-((1-H-indol-3-iyl) (phenyl) methyl)) -1-H-Indol	Triton X-114	THF	FAAS	1.47 ng mL^{-1} Mg 3 ng mL^{-1} Ag	0.007–0.200 μg mL^{-1}	30	Well, spring, tap and mineral drinking water, blood serum, urine, radiology film sample	[221]
Cu, Ni	3-[(8-{[(E)-2-hydroxyimino-1-methylpropylidene] amino}-1-naphthyl) imino]-2-butanone oxime	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	FAAS	0.14 ng mL^{-1}Cu 0.2 ng mL^{-1}Ni		65 Cu 59 Ni	Natural water	[222]
Ag, Cd	Benzylbis (thiosemicarbazone)		0.1 mol L^{-1} HNO_3 in methanol	FAAS	0.04 ng mL^{-1} Ag 0.08 ng mL^{-1} Cd		140 Ag 60 Cd	Natural water	[223]
Ni, Cu, Co	N(2-thiophenyl)-1-(2-hydroxyphenyl)imine	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	1 ng mL^{-1} Ni 5 ng mL^{-1} Cu 6 ng mL^{-1} Cd	0.007–0.33 μg mL^{-1}	30	Tap and well water, chocolate, honey	[224]

in their spectroscopic characteristics following changes in pH and solvent (pH of solvent polarity indicators) [202,203].

The common structural feature of these compounds is the azomethine group with a general formula RHC═N–R′, where R and R′ are alkyl, aryl, cycloalkyl or heterocyclic groups which may be variously substituted. Presence of a lone pair of electrons in an sp^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical importance and imparts excellent chelating ability, especially when used in combination with one or more donor atoms (especially from functional groups like –OH or –SH) close to the azomethine group. In such cases, Schiff bases can form water insoluble complexes with the metal ion with a five- or six-membered ring. Chelating ability combined with the ease of preparation, flexibility in varying the chemical environment about the C═N group and their insolubility in aqueous solution makes Schiff bases interesting ligands from the point of CPE preconcentration.

However, most Schiff bases show a tendency to be involved in various equilibria, like tautomeric interconversions, hydrolysis, or formation of ionized species [204,205]. Moreover, they are chemically unstable and decompose easily in acidic solutions, limiting their use to weak acidic and basic conditions. Therefore, successful application of Schiff bases requires a careful study of their characteristics [206].

In Table 8 we present some CPE methods based on Schiff base complexes with metal ions. As can be seen, the Schiff bases constitute another family of powerful chelating agents utilized in CPE, due to the fact that they are easy to synthesize and have structural rigidity, and they form complexes with high hydrophobicity.

8. Other reagents used for CPE preconcentration of metal ions

Besides the above-described groups of ligands, other complexometric organic reagents are also applied to the preconcentration of metal ions. Typically, they are used in single, rarely in more, CPE procedures, such as 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP). For this reason, to systematize and summarize these reagents in Table 9, we divided them into three groups: ketones, organic acids and organic bases, according to functional groups which enable their interactions with the determined metal ions. Approximately 43% of the developed procedures are based on complexes of metal ions with ketones, 33% with organic bases, and acid ligands are applied in 24% of the developed methods. Among the organic reagents used in CPE, we can find some that are considered as truly "basic" as regards their chemical structures and analytical properties such as sensitivity, selectivity, etc. The other complex-forming compounds are mainly analogs of these "basic" reagents and they usually offer a slight enhancement of analytical properties. This enhancement is not higher than 2- or 3-fold, so taking into account their preparation costs (they are usually more expensive) and accessibility, it is not always reasonable to synthetize them, especially when they are used only once [296].

9. Conclusion and future trends.

Application of complexometric organic reagents in analytical chemistry has a long history. They have played a significant role both in the development of theoretical concepts in this area of science and in practical chemical analyses of many inorganic and organic species. Moreover, their use is combined with qualitative and quantitative determination of different compounds using various analytical techniques such as spectrophotometry, atomic

Table 9
Other organic reagents used for CPE preconcentration of metal ions.

Ion	Reagent	Micellar system	SRP diluting agent	Detection system	DL	Linearity	PF	Matrix	Ref.
Ketones									
Cd	PMBP	Triton X-100	0.1 mol L^{-1} HNO_3 in methanol	FAAS	0.64 ng mL^{-1}	6–100 ng mL^{-1}	23	Tap and lake water	[225]
Mn	PMBP	Triton X-100	0.1 mol L^{-1} HNO_3 in methanol	FAAS	1.45 ng mL^{-1}	5–120 ng mL^{-1}	20	Tap and lake water	[226]
Ni	PMBP	Triton X-100	0.1 mol L^{-1} HNO_3 in methanol	GFAAS	0.12 ng mL^{-1}	Up to 300 ng mL^{-1}	27	Tap and lake water	[227]
Pb	PMBP	Triton X-114	Methanol	FAAS	1.49 μg L^{-1}	5–200 μg L^{-1}	110	Waste, rain, and tap water, human hair, urine, cow liver	[228]
Cr	PMBP	Triton X-114	0.1 mol L^{-1} HNO_3	GFAAS	21 ng L^{-1}	Up to 100 ng mL^{-1}	42	Tap and lake water	[229]
Al	PMBP	Triton X-114	0.1 mol L^{-1} HNO_3	GFAAS	0.09 ng mL^{-1}	Up to 90 ng mL^{-1}	37	Tap and lake water, human urine, human hair	[230]
Au, Pd	PMBP	PONPE 7.5	0.1 mol L^{-1} HCl in methanol	FAAS	3.8 μg L^{-1} Au 1.8 μgL^{-1} Pd	0.004–0.5 μg mL^{-1} Au 0.004–0.5 μg mL^{-1} Pd	16 Au 17 Pd	Geological samples-mine and ore	[231]
Al	Morin	Triton X-114	Ethanol–water mixture (1:1)	SPF	0.24 μg L^{-1}	10–100 μg L^{-1}	20	Drinking water, scalp hair	[232]
Al	Morin	Triton X-114	Ethanol–water mixture (1:1)	SPF	0.34 μg L^{-1}	10–100 μg L^{-1}	25	human hair, dialysate solution	[233]
Ge	Quercetin	Triton X-114	HCl	HGAAS	0.59 μg L^{-1}		200	Deionized, tap and commercial drinking water	[234]
Cr	Luminol	Triton X-114 and SDS		Chemiluminescence	0.5 ng L^{-1}	2–200 ng L^{-1}		Sea, river and waste water	[235]
Cr	Dibromophenylfluorone	Triton X-100	1 mol L^{-1} HNO_3 in methanol	ETAAS	quantitation limit 0.01 μg L^{-1} Cr(VI)	0.5–10 μg L^{-1}	50	Tap, river and lake water	[236]
Cr	Phenylfluorone	CTAB	Ethanol	Spectrophotometry	1.04 μg L^{-1}	5–100 μg L^{-1}	11.3	Lake, sea and electroplating waste water	[237]
W	Salicylfluorone	Triton X-100	Water	SPF	0.14 ng mL^{-1}	0.8–20 μg L^{-1}		Soil	[238]
Hg	TMK	Triton X-114	Ethanol	Spectrophotometry	0.83 ng mL^{-1}	5.0–80.0 ng mL^{-1}	11	Tap, well, river and waste water	[239]
Pd	TMK	Triton X-114	Methanol	Spectrophotometry	0.47 ng mL^{-1}	2–50 ng mL^{-1}	50	Tap, spring and sea water	[240]
Cr	Acetylacetone	Triton X-100	0.1 mol L^{-1} HNO_3 in methanol	FAAS	0.32 ng mL^{-1}	Up to 1000 ng mL^{-1}	35	Tap and lake water	[241]
Cr	Thenoyltrifluoracetone	Triton X-114	0.125 mol L^{-1} HCl in methanol	ETV-ICP-OES	0.22 μg L^{-1}		50	Tap and lake water	[242]
Cd, Co, Cr, Cu, Fe, Mn	Thenoyltrifluoracetone	Triton X-114	0.5 mol L^{-1} HNO_3 in propanol	ICP-OES	0.1 μg L^{-1} Cd 0.3 μg L^{-1} Co 0.2 μg L^{-1} Cr 0.4 μg L^{-1} Cu 2.2 μg L^{-1} Fe 0.1 μg L^{-1} Mn	5–250 μg L^{-1} Fe, 0.5–100 μg L^{-1} Cd, Co, Cr, Cu, Mn	71 Cd 97 Co 81 Cr 96 Cu 42 Fe 60 Mn	Tap, well, sea and mineral water	[243]
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	Thenoyltrifluoracetone	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	ICP-OES	0.028 μg L^{-1} La 0.099 μg L^{-1} Ce 0.103 μg L^{-1} Pr 0.020 μg L^{-1} Nd 0.018 μg L^{-1} Sm 0.014 μg L^{-1} Eu 0.013 μg L^{-1} Gd		14 La 10 Ce 14 Pr 11 Nd 10 Sm 9 Eu 12 Gd	Mineral water, river water	[244]

Table 9 (*continued*)

Ion	Reagent	Micellar system	SRP diluting agent	Detection system	DL	Linearity	PF	Matrix	Ref.
					0.047 μg L^{-1} Tb 0.015 μg L^{-1} Dy 0.009 μg L^{-1} Ho 0.022 μg L^{-1} Er 0.003 μg L^{-1} Tm 0.002 μg L^{-1} Yb 0.002 μg L^{-1} Lu		9 Tb 10 Dy 9 Ho 9 Er 10 Tm 11 Yb 12 Lu		
Pt, Pd	1,8-diamino-4,5-bis(hydroxyamino) Anthraquinone	Triton X-114	70% HNO_3	ICP-OES	0.3 μg L^{-1} Pt 0.45 μg L^{-1} Pd	0.4–1200 μg L^{-1} Pt 0.6–1000 μg L^{-1} Pd	35.4 Pt 29 Pd	Platinum-palladium spent catalysts	[245]
Cu	5,5′-diphenylimidazolidine-2-thione-4-one	Triton X-114	0.5 mol L^{-1} HNO_3 in methanol	FAAS	1.5 ng mL^{-1}	0.01–1.5 μg L^{-1}	39	Waste, river and tap water, blood, vegetable	[246]
Cr	Trifluoropentanedione for Cr(III)	Triton X-114 and CPB	5% mixture of 1:1 methanol–HNO_3	ICP-OES	0.02 ng mL^{-1} Cr(III) 0.05 ng mL^{-1} Cr(VI)	5–1500 ng mL^{-1} Cr(III) 10–1000 ng mL^{-1} Cr(VI)	50 Cr(III) 15 Cr(VI)	Final effluent, industrial effluent, electronic industry, pharmaceuticals, domestic drainage water	[247]
Mo	1,2,5,8-tetrahydroxyanthracene-9,10-dione	Triton X-114	1 mol L^{-1} HNO_3 and THF	GFAAS	7 ng L^{-1}	0.03–0.6 μg L^{-1}	25	Tap and sea water	[248]
Au, Pd	1,8-diamino-4,5-dihydroxy anthraquinone	Triton X-114	65% HNO_3	ICP-OES	0.5 μg L^{-1} Au 0.3 μg L^{-1} Pd	0.5–1000 μg L^{-1}	8.6 Au 20.2 Pd	Mine stones	[249]
Be	1,8-dihydroxyanthrone	Triton X-114	60:40 Methanol–water mixture containing HNO_3	ICP-OES	0.001 ng mL^{-1}	0.006–80 ng mL^{-1}	16.7	Tap, mineral and sea water	[250]
Ni	Di-2-pyridyl ketone salicyloylhydrazone	Triton X-114	0.1 mol L^{-1} HNO_3 in ethanol for GFAAS and FAAS; ethanol for spectrophotometry	GFAAS, FAAS, spectrophotometry	0.14 μg L^{-1} GFAAS 0.76 μg L^{-1} FAAS 1.5 μg L^{-1} spectrophotometry	0.25–2 μg L^{-1} GFAAS, 5–50 μg L^{-1} FAAS 2.94–29.4 μg L^{-1} spectrophotometry	27	Water samples, hemodialysis concentrate, urine, honey	[251]
Cd	1,5-bis(di-2-pyridylmethylene)thiocarbonohydrazide	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	FAAS	0.95 μg L^{-1}	At levels near DLs up to 200 μg L^{-1}	10,5	City waste incineration ash, tap and sea water, apple, lettuce, liver, chick-pea, fish, *Bignonia* leaves, *Pinus* leaves, soil	[252]
U	Dibenzoylmethane	Triton X-114	Methanol	Spectrophotometry	11 ng mL^{-1}	15–300 ng mL^{-1}	62	Springer water near the uranium mine	[253]
U, Th, Zr, Hf	Dibenzoylmethane	Triton X-114	20:80 methanol–1 mol L^{-1} HNO_3 mixture	ICP-OES	0.15 μg L^{-1} Hf 0.10 μg L^{-1} Th 1.00 μg L^{-1} U 0.20 μg L^{-1} Zr	0.5–1500 μg L^{-1} Th and Zr 0.5–500 μg L^{-1} Hf 2.5–1240 μg L^{-1} U	39.5 Hf 43.6 Th 37.0 U 41.7 Zr	Well, spring and sea water	[254]
Organic acids									
Ni, Co	ACDA	Triton X-114	DMF	Spectrophotometry	10 μg L^{-1} Ni 7.5 μg L^{-1} Co	20–500 μg L^{-1} Ni 20–200 μg L^{-1} Co		Tap, river, sea and waste water	[255]
Be	Chromazurol S	Triton X-114	THF	Spectrophotometry	0.05 ng mL^{-1}	0.30–18 ng mL^{-1}	25	Tap, mineral and sea water	[256]
Al	Chromazurol S	PONPE 7.5 and BDTAC	Acetonitrile	Spectrophotometry	1.12×10^{-7} mol L^{-1}	$2 \cdot 10^{-7}$–$2.5 \cdot 10^{-5}$ mol L^{-1}	50	Parenteral solutions	[257]
Fe, Cu	Eriochrome Cyanine R	Triton X-114		FAAS	0.33 ng mL^{-1} Fe 0.57 ng mL^{-1} Cu	1.5–25 ng mL^{-1} Fe 1.0–35 ng mL^{-1} Cu	141 Fe 99 Cu	Mineral and sea water, lettuce, cabbage, spinach, tomato, white	[258]

								and multi grain bread, hazelnut, bush, branches and leaves, fortified water	
U	Chromotrope 2R	Triton X-114 and CTAB	DMF	Diode array spectrophotometry	0.035 ng mL^{-1}	0.2 – 10 ng mL^{-1}	20	Tap and well water	[259]
Co	Calcon carboxylic acid	Triton X-114	Acetonitrile	FAAS	0.20 μg L^{-1}	0.7–100 μg L^{-1}	60	Fortified, drinking and tap water, beer, wine	[260]
Sn	Calcon carboxylic acid	PONPE 7.5	1 mol L^{-1} HNO_3 in methanol	FAAS	2.86 μg L^{-1}	10–1300 μg L^{-1}	100	Drinking and tap water, tomato paste, peas, corn, fruit juices and soft drinks	[261]
Tl	Diethylenetriaminepentacetic acid	Triton X-114 and SDS	2% L-cysteine	ICP-MS	0.02 pg mL^{-1}	2–500 pg mL^{-1}	125	Sea, surface, tap water	[262]
Zn	Capric and undecanoic acids with *n*-octylamine	OP-10	Water	FAAS				Tap water	[263]
Cu	Capric acid in the presence of octylamine	OP-10	Water	F-AAS	0.01 μg L^{-1}	0–2 μg L^{-1}		Tap water	[264]
Cd	Capric acid with *n*-octylamine	OP-10	water	FAAS				River and waste water	[265]
Fe, Pb	Bromopyrogallol red	CTAB	DMF	Spectrophotometry	0.02 ng mL^{-1} Fe 0.04 ng mL^{-1} Pb	0.05–43.00 ng mL^{-1} Fe 0.10–40.00 ng mL^{-1} of Pb	20	Lettuce, spinach, cabbage, parsley, dill, tea, rice, human hair, liver, and chicken and water	[266]
Mo	Bromopyrogallol red	CTAB	DMF	Spectrophotometry	0.1 ng mL^{-1}	0.3–320.0 ng mL^{-1}	20	Standard alloy steels, tap and mineral water	[267]
Ba	Carboxyarsenazo	Triton X-100, CPC and octylamine	4% KCl	FAAS	0.02 mg L^{-1}	1–50 mg L^{-1}	25	Water	[268]
U	Pyrocatechol violet	CTAB and Triton X-114	DMF	Spectrophotometry	0.06 ng mL^{-1}	0.2–10 ng mL^{-1}	14.3	Tap, waste and well water	[269]
Al	Xylidyl Blue	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	1.43 μg L^{-1}	5–800 μg L^{-1}	50	Mineral and drinking water	[270]
Cu	Isoleucine	Triton X-100	Methanol	Spectrophotometry	5 μg L^{-1}	10–1000 μg L^{-1}	22	Lake and tap water, rice flour, wheat flour	[271]
Cu	1,2-Dihydroxy-anthraquinone-3-Sulfonic acid	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	FAAS	1.07 ng mL^{-1}	5–200 ng mL^{-1}	21	Tap, fortified and surface water	[272]
Ce	n-p-Tolylbenzohydroxamic acid	Triton X-114	1 mol L^{-1} HNO_3	ICP-OES	0.4 μg L^{-1}	1.5–1200 μg L^{-1}	13.8	Sea, mineral and tap water	[273]
Organic bases									
Sb	BPHA	Triton X-114	Methanol	FAAS	1.82 ng mL^{-1} Sb(III) 2.08 ng mL^{-1} Sb(total)		45	Artificial, sea and natural waste water	[274]
Hg	Methyl green and I^-	Triton X-114	0.5 mol L^{-1} HNO_3	ICP-OES	56.3 ng L^{-1}	0.25–100 μg L^{-1}	56.3	Dogfish mussel, fresh seafood-scallop, razor clam, mussel, creamfish, mackerel	[275]
Cd	Methyl green	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	FAAS	0.9 ng mL^{-1}	2–200 ng mL^{-1}	13.5	Rice, milk powder, walnut powder, laver, kelp	[276]
Pb	Brillant cresyl blue	Triton X-114	1 mol L^{-1} HNO_3 in ethanol	FAAS	7.5 μg L^{-1} water 0.33 μg g^{-1} sediment		25	Mineral and tap water, lake sediment and sewage sludge	[277]
Cr	Brilliant cresyl blue	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	0.42 μg L^{-1}	1.5–70 μg L^{-1}	25	Tap and drinking water	[278]
V	Methylene blue	Triton X-114	2 mol L^{-1} HNO_3	GFAAS	0.7 ng mL^{-1}	4.3–130.0 ng mL^{-1}	10	Soil	[279]
Au	Brilliant green	Triton X-114	Methanol	FAAS	1.5 ng mL^{-1}	3–1000 ng mL^{-1}	31	Granite, silicate rock samples	[280]
Cd	*o*-Phenanthroline and eosin	PONPE 7.5	Buffer Tris pH 7.6	SPF	8.38×10^{-4} μg L^{-1}				[281]

Table 9 (*continued*)

Ion	Reagent	Micellar system	SRP diluting agent	Detection system	DL	Linearity	PF	Matrix	Ref.
						2.79×10^{-3}–2.81 μg L^{-1}		Mineral, tap and well water	
Hg	Rhodamine B	Triton X-114	Water–ethanol (10:1)	Spectrophotometry	1.4 ng mL^{-1}	10–100 ng mL^{-1}	5	Chromplating industry and textile industry effluents, lake and tap water	[282]
As	Pyronine B	Triton X-114		ETAAS	0.022 μg L^{-1}		52	Dialysate solution, scalp hair samples	[283]
Cd	Cadion	Triton X-114		Spectrophotometry				Water	[284]
Cu	4-(phenyl diazenyl) benzene-1,3-diamine	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	0.6 ng mL^{-1}	0.01–0.26 μg L^{-1}	30	Vegetable, liver, meat, lotus (tree), soil, blood, tap water	[285]
Se	2,3-Diaminonaphthalene	Triton X-114	water	SPF	2.1 μg L^{-1}	0.020–0.700 mg L^{-1}	10	Selenium supplement tablets	[286]
Fe, Cu	3-Amino-7-dimethylamino-2-methylphenazine	Triton X-114	0.05 mol L^{-1} H_2SO_4	FAAS	0.7 ng mL^{-1} Fe 0.3 ng mL^{-1} Cu	2.5–200 ng mL^{-1} Fe 1–200 ng mL^{-1} Cu	98 Fe 69 Cu	spice samples: red and black pepper, cumin, cinnamon, mint, thyme	[287]
Se	3,3'-diaminobenzidine	Triton X-114	5% HNO_3	ETAAS	2.5 ng L^{-1}	10–200 ng L^{-1}	100	Tap and ground water, animal blood, fish tissue	[288]
Cu, Zn, Fe, Ni	2-Phenyl-1H-benzo[d] Imidazole	Triton X-114	2 mol L^{-1} HNO_3 in methanol	FAAS	1.8 ng mL^{-1} Cu 2.8 ng mL^{-1} Fe 1.4 ng mL^{-1} Zn 2.1 ng mL^{-1} Ni	0.2–0.26 mg L^{-1}	58 Cu 38 Fe 64 Zn 45 Ni	Bovine liver, blond, lotus (tree), milk, orange juice, apple fruit, fennel	[289]
Pd	6-Nitro-5-methoxy-3-(indoline-2-one)hydrazine carboxyamide	Triton X-114	0.1 mol L^{-1} HNO_3 in methanol	FAAS	0.065 ng mL^{-1}	1.14–4.83 ng mL^{-1}	81	Sea, river, well and tap water, soil, tomato, beans, tobacco, bignonia leaves, pinus leaves	[290]
Pd, Pt, Au	N,N-dihexyl-N′-benzoylthiourea	Triton X-114	1 mol L^{-1} HNO_3 in methanol	ICP-QMS	Seawater 0.01 pg mL^{-1} Pt 0.01 pg mL^{-1} Pd 0.15 pg mL^{-1} Au Road dust 3.1 pg g^{-1} Pt 4.4 pg g^{-1} Pd 44 pg g^{-1} Au	10–1000 pg mL^{-1} Pt 10–500 pg mL^{-1} Pd 40–1500 pg mL^{-1} Au	100 Pt 104 Pd 105 Au	Tap and sea water, road dust, soil	[291]
Cu, Ni, Zn, Fe	3-((indolin-3-yl) (phenyl)methyl)indoline	Triton X-114	2 mol L^{-1} HNO_3 in methanol	FAAS	1.6 ng mL^{-1} Cu 2.8 ng mL^{-1} Fe 2.1 ng mL^{-1} Ni 1.1 ng mL^{-1} Zn	0.01–0.20 mg L^{-1} Zn 0.01–0.30 mg L^{-1} Ni, Fe, Cu	30	Blood, lotus tree, liver, spinach, soil, orange juice	[292]
Mg	Trizma-chloranilate salt	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	0.75 μg L^{-1}	5–220 μg L^{-1}	50	River, sea and mineral waters	[293]
Cd, Cu, Pb, Fe	2,6-diamino-4-phenyl-1,3,5-triazine	Triton X-114	1 mol L^{-1} HNO_3 in methanol	FAAS	0.38 μg L^{-1} Cd 0.48 μg L^{-1} Cu 1.33 μg L^{-1} Pb 1.85 μg L^{-1} Fe	1.50–80 μg L^{-1} Cd 1.25–55 μg L^{-1} Cu 20–320 μg L^{-1} Pb 3.5–140 μg L^{-1} Fe	25	Snow, spring, and tap water, rice flour and tea	[294]
Be, Cr	Cupferron	Triton X-114	1% HNO_3 in ethanol	ETAAS	0.02 μg L^{-1} Be 0.05 μg L^{-1} Cr	0.05–0.25 μg L^{-1} Be 0.1–0.5 μg L^{-1} Cr	20	Tap, river, mineral drinking water	[295]

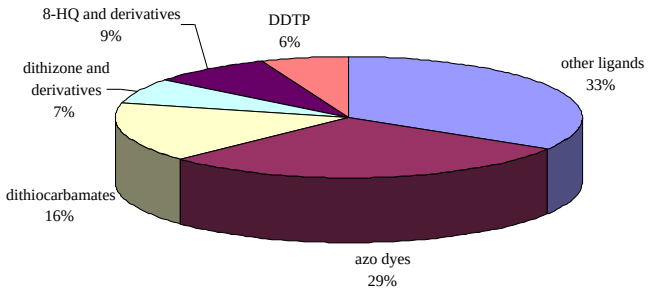


Fig. 12. Frequency of the use of organic ligands in CPE proposed in the past 12 years.

absorption spectrometry, atomic emission spectrometry, voltammetry, capillary electrophoresis or chromatography. They are also useful in auxiliary operations that precede or accompany the analysis, such as masking, preconcentration or separation [296].

In CPE, selection of the complexing agent is the crucial step. The frequency of use of different organic ligands in CPE, which have been proposed over the past 12 years, is shown in Fig. 12. As can be seen, among many kinds of ligands, azo dyes are the most frequently applied ligands due to their low solubility in water and ability to form hydrophobic complexes with a large number of metals. Next to azo dyes are dithiocarbamates. These two groups of reagents are highly versatile complex-forming agents toward main groups of metal ions, and therefore they are widely used in different areas of analytical chemistry.

The low solubility of complex-forming ligands and their metallic complexes in water, most frequently used in CPE, and their ability to form complexes with a large number of metal cations, can still be exploited for developing new, more sensitive determination methods based on systems with multi-element detection, such as ICP-OES, ICP-MS, XRF and some applications for sequential measurements by FAAS. Moreover, these properties can become an advantage when modern, miniaturized separation and preconcentration procedures such as recently much explored liquid–liquid and liquid-phase microextractions or lab-on-chip are applied prior to determination of ultratrace amouts of analyties. However, the future belongs to the combination of these compounds with nanomaterials such as nano-SiO_2, nano-Al_2O_3, nanotubes, graphene, and nanocomposites, especially those which have magnetic properties, for sepatation and preconcentration realized both by off- and on-line systems. Development of such procedures can allow obtaining much lower detection limits and higher preconcentration factors than by using conventional preconcentration procedures.

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