Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 997 (2003) 41–50
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Rapid determination of ions by combined solid-phase extraction–diffuse reflectance spectroscopy

James S. Fritz*, Matteo P. Arena, Steven A. Steiner, Marc D. Porter
Microanalytical Instrumentation Center, Ames Laboratory, U.S. Department of Energy, and Department of Chemistry, Iowa State University, Ames, IA 50011, USA

Abstract

We introduce colorimetric solid-phase extraction (C-SPE) for the rapid determination of selected ions. This new technique links the exhaustive concentration of an analyte by SPE onto a membrane disk surface for quantitative measurement with a hand-held diffuse reflectance spectrometer. The concentration/measurement procedure is complete in ~1 min and can be performed almost anywhere. This method has been used to monitor iodine and iodide in spacecraft water in the 0.1–5.0 ppm range and silver(I) in the range of 5.0–1000 μg/l. Applications to the trace analysis of copper(II), nickel(II), iron(III) and chromium(VI) are described. Studies on the mechanism of extraction showed that impregnation of the disk with a surfactant as well as a complexing reagent results in uptake of additional water, which markedly improves the extraction efficiency.

Keywords: Colorimetric solid-phase extraction; Extraction methods; Diffuse reflectance spectroscopy; Detection, solid-phase extraction; Metal cations

1. Introduction

Space exploration by humans requires an adequate supply of drinking water. Small amounts of either iodine (up to 3 mg/l) or silver(I) (up to 0.5 mg/l) are added to the water to prevent growth of harmful bacteria and ensure that the water is safe for human consumption. Periodic monitoring of iodine or silver(I) in the water is necessary to ensure that the concentration level is in the desired range. The testing method must be simple, rapid and applicable to conditions of microgravity.

There are several approaches for potentially meeting these needs. One possibility uses reagent-impregnated materials that react with an analyte to produce a colored complex. The most basic version of this approach is based on the immersion of an impregnated strip into a sample and estimating the analyte concentration from the intensity of the immobilized colored complex. However, the color intensity is dependent not only on the analyte concentration but also on the equilibrium constant for complexation and on the immersion time. Equilibrium is sometimes reached only after extended immersion.

In cases in which the analytes are present at very low concentrations it may be necessary to use a preconcentration step in order to achieve the requisite limit of detection. A convenient approach to meeting this need is solid-phase extraction (SPE), which can achieve concentration factors of 1000 or more. In its most rudimentary form, a sample is

*Corresponding author. Tel.: +1-515-2945-987; fax: +1-515-2943-578.
E-mail address: kniss@ameslab.gov (J.S. Fritz).

0021-9673/03/$ – see front matter
doi:10.1016/S0021-9673(03)00551-X

passed through a disk impregnated with a complexing reagent. The target sample analyte is extracted by the disk, forming a colored complex. The amount of analyte on the disk is then determined by color comparison with standards or by diffuse reflectance spectroscopy (DRS). This strategy has been employed for the determination of phosphate by the molybdenum blue method [1], uranium(VI) as the thiocyanate complex [2], and cobalt and platinum ions as pyridylazoresorcinol (PAR) complexes [3]. Preformed complexes of silver and platinum ions [4] and zinc ions [5] have been preconcentrated on disks impregnated with vinylpyridine groups.

We recently introduced an intriguing simplification of this methodology: colorimetric solid-phase extraction (C-SPE) [6]. With C-SPE, a membrane is placed in a holder and the disk is directly impregnated with the colorimetric reagent. A syringe containing a measured volume of sample is attached to the holder and the sample is passed through the disk, forming an analyte–reagent colored complex on the disk. The amount of analyte is measured directly on the disk surface by DRS using a small hand-held instrument. By using a membrane disk containing polystyrene–divinylbenzene particles impregnated with polyvinylpyrrolidone (PVP), we demonstrated that iodine could be exhaustively extracted from aqueous solution as a yellow iodine–PVP complex and measured quantitatively by DRS. The sample work-up and readout time totaled only ~60 s. With a 10-ml sample a linear calibration plot was obtained, yielding an iodine detection limit of 0.05 mg/l.

More recently, the concept of C-SPE has been extended to the rapid, trace-level (~4 μg/l) monitoring of silver(I), the biocide presently used on the international space station [7]. The determination relies on passage of a sample through a membrane disk that has been impregnated with the colorimetric reagent 5-(*p*-dimethylaminobenzylidine)rhodanine (DMABR) and an additive such as 1,2-decanediol or a non-ionic surfactant (Brij 30).

C-SPE is by no means limited to analysis of spacecraft water for iodine and silver(I). This approach should be considered for any case where a rapid determination is needed for low concentrations of a given analyte in aqueous samples. By combining preconcentration by SPE and rapid measurement by DRS into a single integrated method, C-SPE can give a very low limit of detection. It is also well suited to on-site analyses. We now review the principles of C-SPE and survey the possibilities for ion analysis. Preliminary results are given for entirely new methods for copper(II), nickel(II) and several other ions.

2. Experimental

2.1. Reagents and chemicals

All solutions were prepared with deionized water that was further purified by a Nano-Pure water-purification system (Barnstead). Metal ion solutions were prepared from reagent grade salts. Stock solutions containing 1.0 g/l of the metal ion were prepared from the nitrate salts of the following metal ions: silver(I), copper(II), nickel(II) and iron(III). Stock solutions containing 0.20 g/l of iodine and 1.0 g/l iodide were also prepared. Standard solutions of lower concentrations were prepared daily by dilution of the stock solutions. Oxone solution for oxidation of iodide was prepared by dissolving 0.10 g of Oxone (Aldrich) in 100 ml of water.

2.2. Membrane disk preparation

The extraction membranes were prepared by impregnating Empore SDB-XC (3M) polystyrene–divinylbenzene 47-mm extraction disks with appropriate reagents. This process was carried out by mounting a membrane on a Millipore 47-mm all-glass vacuum filter holder and pulling the impregnating reagent solutions through by vacuum. Residual solution was removed by vacuum for an additional 1–2 min. Then, the membranes were cut into 13-mm disks by means of a cork borer.

The following impregnating solutions were used:

For iodine: 10 ml of a solution containing 30 g/l of polyvinylpyrrolidone (average M_w~10 000, Aldrich) in water–methanol (1:1).

For silver(I): 10 ml of a 2-g/l solution of DMABR (Aldrich), 30 g/l in methanol–dimethylformamide (1:9). Then pass through 5 ml of a Brij 30 (Aldrich) solution, 30 g/l, in water.

For copper(II): 10 ml of a solution containing 0.40

g/l of zinc diethyldithiocarbamate (Zn DTC) in water. Dry for 2 h after impregnation.

For nickel(II): cut Whatman GF/C glass microfibre filters into 13-mm diameter disks, then spread ~4 mg of a dry mixture of 2.0 g starch and 0.10 g nioxime evenly onto the surface.

For iron(III): 10 ml of 50 g/l 8-hydroxy-7-(6-sulfo-2-naphthylazo)5-quinolinesulfonic acid, disodium salt (SNAZOXS). Then, 10 ml of 30 g/l of cetylpyridinium chloride (CPC) in water.

For chromium(VI); 10 ml of 30 g/l cetylpyridinium chloride in water.

2.3. Instrumentation

A BIK-Gardner color-guide sphere d/8° diffuse reflectance spectrophotometer (Model No. LCB-6830, Bik-Gardner) was used to collect all spectral data from the membrane materials. This hand-held spectrophotometer is small, light in mass, battery operated, and can collect reflectance data over the entire visible spectral range (400–700 nm) in 20-nm increments in only 1.5 s. The entire spectrum is displayed on the instrument readout panel. The small aperture of the instrument enables reflectance readings to be made on a 13-mm diameter disk. The sample are mated to the spectrometer by means of the sample positioning housing of the instrument.

The 13-mm membranes were mounted in 13-mm plaster Fisherbrand SyringeSwinnex Filter Holders (Catalogue No. 09-753-10ASX00 0013 00, Fisher Scientific Millipore). A 10-ml plastic syringe containing 10.0 ml of sample was connected to the holder in order to extract the analyte from the sample by its passage through the membrane.

2.4. Software

The spectrophotometer was interfaced to a personal computer using a serial cable. The spectra were transferred to the personal computer and downloaded to the color-guide MS-Excel worksheet for the instrument in order to plot the reflectance data from 400 to 700 nm. The data were then transferred to another Excel worksheet to calculate the Kubelka–Munk functions and plot calibration curves.

2.5. Procedure for extraction and readout

The following procedure is valid for all the considered metals except for nickel.

A 10-ml or 2-ml plastic syringe was loaded with the desired volume of aqueous sample. A 13-mm membrane disk, impregnated as described above, was placed on the plastic support screen of the holder and the top section of the holder was tightly screwed. The plastic syringe loaded with sample was attached to the holder via a Luer-lock fitting and the sample was pushed manually through the disk in the holder at a rate of approximately one drop per second. This step required 15–30 s. After the extraction, ~10 ml of air was passed through the holder to remove remaining sample. Then, the holder was detached from the syringe and unscrewed. The disk was removed from the holder and placed under a sample area locator, the DRS instrument was placed on the disk and the trigger pushed to acquire the sample spectrum. The reflectance at the analytical wavelength was used to calculate the Kubelka–Munk function, $F(R)$.

For the determination of nickel(II) the following preliminary step was used to add nioxime to the sample. A glass fiber disk treated with nioxime–starch was placed in a holder and the holder connected to an empty plastic syringe. The sample was drawn through the holder to fill the syringe. Then the syringe was detached from the holder and re-attached to a second holder containing the Empore disk used for the SPE.

3. Results and discussion

3.1. Principles of colorimetric SPE

C-SPE was developed initially to provide a rapid, reliable way to monitor 0.1–5-mg/l levels of iodine in spacecraft drinking water. The membranes, equipment, and basic procedure are described in the Experimental section. Basically, an aqueous sample is pulled through an extraction disk impregnated with a reagent (PVP, in this instance) that simultaneously concentrates the desired analyte (iodine) and enables the development of a color (iodine-PVP) due to complexation of the analyte with the reagent. The

amount of colored analyte complex on the upper surface of the disk is then determined by a hand-held diffuse reflectance spectrometer. The instrument acquires the reflectance (R) percentages between 400 and 700 nm in 20-nm intervals and stores them for processing of the data by a laptop computer. These measurements are complete in only ~2 s.

The Kubelka–Munk (KM) equation provides an effective approach for converting the absolute diffuse reflectance to a form that will give a linear calibration plot for quantitative measurements [8]. The Kubelka–Munk function $F(R)$ is defined as:

$$F(R) = (1 - R)^2/2R$$

This function is directly related to the concentration of an absorbing sample species, C, by:

$$F(R) = \varepsilon C/s$$

where ε is the molar absorptivity of the sample species and s is the scattering coefficient of the sample surface. Thus, a linear plot is expected for $F(R)$ as a function of the concentration of the absorbing sample species.

Application of the Kubelka–Munk equation in C-SPE is illustrated by the determination of iodine [6]. Iodine may be extracted as molecular iodine, with a maximum of 500 nm in the diffuse reflectance spectrum, or as the iodine–PVP complex, which has a significantly higher maximum at 420 nm. Complexation of iodine with PVP also reduces volatility losses of iodine from the surface of the disk. A linear calibration plot for $F(R)$ vs. iodine was obtained at 420 nm with PVP impregnated disks in the 0.1–1.0-mg/l concentration range. By working at 440 nm, a linear plot was obtained between 0.1 and 5.0 mg/l.

In conventional solid-phase extraction an analyte is extracted onto a membrane disk or loose particles in a tube. The elution step is usually accomplished by means of an organic solvent, an acidic aqueous solution, or by thermal desorption. The present method is quicker and more convenient than traditional SPE in that the extracted analyte is measured directly on the membrane surface by reflectance spectroscopy, eliminating the need for an elution step. However, the performance criteria for effective C-SPE are somewhat more demanding than those necessary for more conventional modes of SPE. Both methods require a high retention factor so that essentially all of the analyte will be retained on the SPE disk. With C-SPE, the analyte must be retained as a thin layer at or near the upper surface of the disk, which limits the overall dynamic range to ~2 orders of magnitude. This requirement arises from the fact that diffuse spectroscopy has a limited depth sensitivity [9]. Therefore, any portion of the analyte retained on the disk below the light penetration depth will not be detected. Being a colorimetric technique, C-SPE also requires that the analyte or the resulting complex be a chromophore.

The membrane disks used in C-SPE are very efficient extraction media. They contain particles of an average diameter of 40 μm, or in some cases 20 μm, closely packed within the teflon membrane disk. Although the disk has a relatively small thickness, it is estimated that at least 20 theoretical plates are generated when a sample is passed through the disk [10]. A distribution constant, K_d, of 1000 or more is commonly attainable in SPE [10]. The breakthrough volume, V_R, of an analyte will depend on the extraction capacity of the disk as well as K_d. For samples of very low analyte concentration, V_R can be estimated from K_d as in the following example. For a disk 10 mm in diameter, 1.0 mm thick with a void volume:solid volume of 1:3 within the membrane disk:

$$V_o \text{ (void volume of disk)} = (0.5^2\ \pi\ (0.1)/3 = 0.026 \text{ ml}$$

$$k' \text{ (retention factor)} = 3\ K_d = 3000$$

$$V_R \text{ (retention volume)} = V_o(1 + k') = 0.026(3001) = 78.0 \text{ ml}$$

From plate theory,

$$N = \frac{(V_R)^2}{\sigma^2}; \quad \sigma^2 = (78)^2/20 = 304; \quad 2\sigma = 35 \text{ ml}$$

The breakthrough volume (V_B) can be estimated as follows [10]:

$$V_B = V_R - 2\sigma = 78 - 35 = 43 \text{ ml}$$

If the extracted analyte is to be retained on the upper 15% of the membrane thickness, a sample volume of 43×0.15, or ~6.5 ml can be accommodated.

The concentration factor (CF) in SPE is the ratio of the volume of initial sample (V_S) to the volume occupied by the extracted analyte in the disk (V_A). As an example, a physical picture of the layer formed by the silver(I)–DMABR complex within the disk was obtained by carefully slicing a section of a disk, mounting it on a glass slide, and examining the section by fluorescence microscopy [7]. The photomicrograph obtained after 10 ml of an 80-μg/l silver(I) solution was passed through an impregnated disk showed a silver(I)–DMABR layer ~0.15 mm thick. The thickness of the entire membrane disk was 0.62 mm. The volume occupied by the complex, V_A, was calculated from the thickness of the layer and the diameter of the disk (10 mm) to be ~0.012 ml. Thus, $CF = V_S/V_A = 10/0.012 = 833$. Although results may vary with the analyte–complex system and other conditions, a CF between 100 and 1000 is a reasonable expectation in C-SPE.

The extraction capacity of a membrane disk must also be considered. If the amount of extracted substances is too close to the capacity of the disk, breakthrough may occur and the analyte will be spread throughout the disk instead of being concentrated near the upper surface. However, C-SPE is designed for determination of analytes in the μg/l to low mg/l concentration range. The amount extracted can be kept within a desired range by adjusting the volume of sample taken for analysis.

A high degree of selectivity is essential in any analytical method in which a quantitative measurement is based on the spectral properties of an analyte or one of its complexes. To determine a given metal ion by C-SPE, it will usually be necessary to find a reagent that forms an extractable complex with a reasonably high molar absorptivity. An additional requirement is that other metal ions likely to be in the sample should not form a complex of similar color under the same conditions. An auxiliary complexing reagent, often called a ''masking'' agent, can sometimes be added to attain the needed selectivity. The extensive literature of classical spectrophotometry provides a rich source of information that can be used to develop methods for C-SPE.

The kinetics of a complexation reaction used in C-SPE needs to be considered because some reactions occur more rapidly than others. The analyte must react completely with the impregnated reagent during the short time interval in which the reactants are in contact. The flow-through nature of the technique ensures an intimate interfacial contact that is conducive to efficient mass transfer. In addition, the concentration of impregnated reagent on the membrane disk is much higher than would be the case if the reagent were simply added to the sample solution. This condition encourages both a faster and more complete reaction with the selected analyte.

The type of disk selected and the chemical environment within the disk can have a profound effect on C-SPE methods that involve complexation. In the method for silver(I) it was discovered that DMABR is strongly retained by ordinary filter paper and does not detectably elute when washed with water. Although a colored complex is slowly formed when an aqueous solution of silver(I) is passed through an impregnated paper disk, this system is unsuitable for determination of silver(I) because of its slow kinetics and low extraction efficiency. DMABR is also strongly retained by cellulose phosphate paper. The negatively charged phosphate group holds the regent by ion-pair interaction with the protonated dimethylamino group. This interaction leaves the heterocyclic ring of DMABR available for complexation of silver(I). C-SPE with DMABR-impregnated cellulose phosphate is extremely sensitive for silver(I). A linear plot of $F(R)$ vs. concentration was obtained for 10-ml samples containing 5–500 μg/l. Although this system is reasonably satisfactory, the irregular surface of the disks led to poor reproducibility.

Membrane disks containing cross-linked polystyrene particles were found to strongly retain DMABR, but passage of a silver(I) solution through the impregnated disk gave no detectable color change. It appears that the polymeric particles in the disk bind DMABR so strongly that its chelating groups are not free to react with the silver(I). We then hypothesized that impregnation of the membrane with an aliphatic alcohol might create a more hydrophilic environment at the membrane-sample interface that could restore the ability of the DMABR to complex silver(I). Indeed, by impregnation of the disk with DMABR and then with either *n*-octanol, 1,2-decanediol, or with Brij 30 (a nonionic surfactant), silver(I) could be readily complexed and retained when an aqueous sample was

passed through the disk. Subsequent measurement by DRS gave linear plot of $F(R)$ vs. the concentration of silver(I) [7].

The uptake of Brij 30 by a membrane impregnated with DMABR was determined by the change in mass of the membrane. No change in mass was observed after passing 10 ml of water through the disk and drying it under vacuum for 1 min. However, passage of 5 ml of a 30-mg/l solution of Brij 30, followed by 1-min of vacuum produced a mass gain of 61%. This can be attributed to uptake of Brij 30 plus water. After 2 h at 20 °C the water taken up had totally evaporated. However, additional water was taken up when 10 ml of water was passed through the disk and the surface water was removed by 1-min of vacuum. The membrane disk retained ~24% of its mass in Brij 30 and another 37% of its mass in water. Microscopic measurements showed a 17.8% increase in membrane thickness due to the uptake of Brij 30 and water.

Diffuse reflectance spectra of a membrane impregnated with DMABR were run after various treatments. A large increase in reflectance of the upper surface of the membrane was observed after the membrane had been treated with Brij 30. The increase in reflectance is accompanied by a shift from 470 to 460 nm in the maximum reflectance wavelength. These spectral changes as well as the observed swelling of the membrane suggest that Brij 30 has effected a change in the environment around the DMABR.

A membrane disk can also be impregnated with an ionic surfactant in order to bring about a change in selectivity. Thus, picric acid (2,4,6-trinitrophenol) exists in solution primarily as an anion that is only slightly extracted by a polystyrene membrane disk. By impregnating the disk with the cationic surfactant CPC, picrate is attracted to the positive charge on the CPC and is completely extracted as a yellow layer on the upper surface of the disk. Most likely, the CPC also enhances the extraction efficiency by inducing the uptake of additional water by the disk.

3.2. Ion analysis by C-SPE

Several methods for determination of a specified analyte are described in this section. For convenience, the major conditions and performance data for each determination are outlined in Table 1.

3.2.1. Iodine and iodide [6]

Iodine can be extracted exhaustively onto a membrane disk as molecular iodine or onto a disk impregnated with PVP as the iodine–PVP complex. The latter system gives significantly better sensitivity and also inhibits the loss of iodine by sublimation from the uppermost surface of the disk. A gradual linear decline in reflectance is observed even when

Table 1
Summary of methods for ion analysis

Analyte	Reagents	Wavelength (nm)	Linear range (mg/l)	Interferences
Iodine	PVP	440	0.1–5.0	Bromine
Iodide	PVP, Oxone	440	0.1–5.0	Oxidants
Silver(I)	DMABR, Brij 30	540	0.005–0.060 (2-ml sample)	Cl^-, Br^-, I^-, $S_2O_3^{2-}$
		580	0.05–1.0 (10-ml sample)	
Copper(II)	Zn DTC	420	0.005–0.10 (2-ml sample) 0.005–0.030 (10-ml sample)	Ag^+
Nickel(II)	Cyclohexane-dioxime		0.020–0.50	
Iron(III)	SNAZOXS	640	1.0–10.0	

In each case a disk 12 mm in diameter was cut from an Empore SDB-XC membrane and used in conjunction with the holder and syringe described in the Experimental section. Spectral data from the membrane disks were collected using a BIK-Gardner diffuse reflectance spectrometer.

iodine is extracted as the PVP complex but this sublimation is not enough to affect the analysis provided the reflectance is measured within a set time, such as 1–2 min.

The temperature of the water sample has a significant effect on the observed value of $F(R)$. After an initial increase in $F(R)$ for a 0.5-mg/l iodine solution from 0.16 at 4 °C to 0.24 at 10 °C, there is a steady decrease at higher temperatures. Measurements are best made in the reasonably flat portion of the plot between 15 °C ($F(R)=0.20$) and 23 °C ($F(R)=0.17$).

In aqueous solution iodine and iodide coexist through the following equilibrium:

$$I_2 + I^- \leftrightharpoons I_3^-$$

However, for the iodine concentration range of 1.0–5.0 mg/l, tests showed that the presence of iodide, even in considerable excess, had no detectable effect on the determination of iodine. Owing to the low value of the equilibrium constant (7.00×10^2), the equilibrium is easily shifted so that all of the iodine is extracted in the molecular form and none of the iodide is extracted.

Iodide is instantly oxidized to iodine by adding 0.10 ml of a 1-g/l Oxone solution to 10 ml of water sample in the pH range between 4.0 and 7.5. The resulting iodine is then determined by C-SPE. The calibration plots of $F(R)$ vs. concentration were virtually identical for iodine and for iodide.

By using Oxone, it is feasible to analyze mixtures of iodine and iodide containing low concentrations of each. Iodine is determined first, then the sum of iodine plus oxide is determined after oxidation by Oxone. The amount of iodide in the sample is then calculated from the difference in the two values.

3.2.2. Silver(I) [7]

DMABR, which is one of the most popular reagents for colorimetric measurement of silver(I) in solution [11], can also be used in C-SPE. However, the membrane disk must be impregnated with 1,2-decanediol of Brij 30 as well as DMABR in order to create an environment within the membrane in which the DMABR is free to react with silver(I) in the aqueous sample. The basic details of the method are outlined in Table 1. The best linearity of plots of $K(R)$ against silver(I) concentration from 0.05 to 1.0 mg/l was obtained at 580 nm with 10-ml samples. By working at 540 nm where the sensitivity is greater and using 2.0-ml samples, a linear plot was obtained at the very low range of 5–60 μg/l. Under these conditions the calibration plot levels off at higher concentrations.

3.2.3. Copper(II)

Dithiocarbamates and especially sodium diethyldithiocarbamate [12] and ammonium pyrrolidinedithiocarbamate [13] have long been used for colorimetric determination of copper(II) and certain other metal ions. Sodium bis(2-hydroxyethyl)dithiocarbamate forms complexes that are water soluble but can be concentrated effectively by SPE [14]. Table 2 shows that many metal ions can be exhaustively extracted over a broad pH range. Addition of EDTA to the sample as a masking agent prevents any detectable extraction of the iron(III), nickel(II) and zinc(II) dithiocarbamates but does not reduce the percentage extraction of bismuth(III) copper(II), mercury(II) or silver(I).

Copper(II) forms a dithiocarbamate (DTC) complex that is highly colored and is more stable than the DTC complexes of most other metal ions. A membrane disk impregnated with zinc diethyldithiocarbamate (and still moist) can be used in the determination of copper(II) by C-SPE. The logarithm of the extraction coefficient in a chlorinated solvent is 13.7 for copper(II) DTC and 3.0 for zinc(II) DTC. When a solution of copper(II) comes in contact with Zn DTC, the following displacement reaction takes place:

Table 2
pH Range for 100% retention of metal-bis(2-hydroxyethyl)dithiocarbamate complexes by solid-phase extraction onto XAD-4 particles

Ion	pH Range	Ion	pH Range
Bismuth(III)	1–10	Nickel(II)	4–10
Cadmium(II)	4–10	Silver(I)	4–10
Cobalt(II)	1–10	Thallium(I)	1–10
Copper(II)	1–10	Tin(II)	1–10
Iron(III)	5–8	Uranium(VI)	6–7
Lead(II)	1–10	Vanadium(V)	3–7
Mercury(II)	1–10	Zinc(II)	5–9
Molybdenum(VI)	3–4		

$$Cu^{2+} + Zn\,DTC \rightarrow Cu\,DTC + Zn^{2+}$$

The use of Zn DTC, instead of Na DTC, enhances the selectivity of the method in that only the few ions that form the most stable DTC complexes will undergo this displacement reaction.

Fig. 1 (top) depicts the diffuse reflectance spectra of the Cu DTC resulting from passage of different concentrations of copper(II) solutions through a disk impregnated with Zn DTC. The calibration plot for 10-ml samples, shown in Fig. 1 (bottom), has a detection limit of approximately <1 or 1 μg/l for copper(II). At the same wavelength (420 nm) a linear plot was obtained for 2-ml samples over the range <1 to 100 μg/l of copper(II).

3.2.4. Nickel(II)

A class of reagents known as the *vic*-dioximes has been considered to be nearly ideal for determination of nickel(II) [15]. Actually, copper(II) forms a more stable complex with dimethylglyoxime (log $B_2 =$ 19.2) than nickel(II) (log $B_2 = 17.5$), and the cobalt(II) complex is of similar stability (log $B_2 = 17.7$). However, only nickel(II) and palladium(II) form square planar complexes, which have a vivid, distinctive color. Nioxime (cyclohexane-1,2-dioxime) gives much the same photometric reactions as dimethylglyoxime, but nioxime is more soluble in water (~8 g/l) and reacts with nickel(II) at a more acidic pH.

We attempted to determine nickel(II) by passing an aqueous sample through a membrane disk impregnated with nioxime, but no apparent color was observed on the disk. However, addition of nioxime to the sample prior to passage through the disk produced a pink/purple color on the surface of the disk that was proportional to the concentration of nickel in the sample. In field testing it is not always convenient to measure out and add a given amount of reagent to the sample as a preliminary step in the analysis. A convenient answer to this problem is to use a pre-prepared Whatman GF/C glass microfibre filter, coated with a solid mixture of soluble starch (2.0 g) and solid nioxime (0.1 g), and contained in the same type of plastic holder used for C-SPE. An appropriate quantity of nioxime is added when the aqueous sample is sucked through the coated filter into a syringe. Then the microfibre filter is quickly replaced by a holder containing an Empore SDB-XC 47 extraction disk and the measured volume of treated sample is pushed through the disk.

The best way to determine nickel(II) by this procedure was to buffer the initial sample at pH 6.1 with sodium acetate and acetic acid. After introducing the nioxime and passing a 9.0-ml sample through the membrane disk, the diffuse reflectance was measured at 540 nm. As shown in Fig. 2, a smooth calibration plot was obtained in the range of 0–600 μg/l of nickel(II). Each point on the plot was

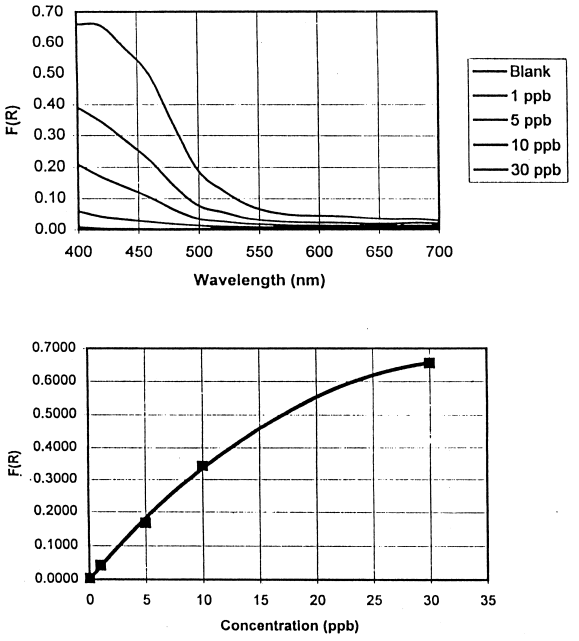

Fig. 1. Top: copper DTC reflectance spectra; bottom: copper(II) calibration plot.

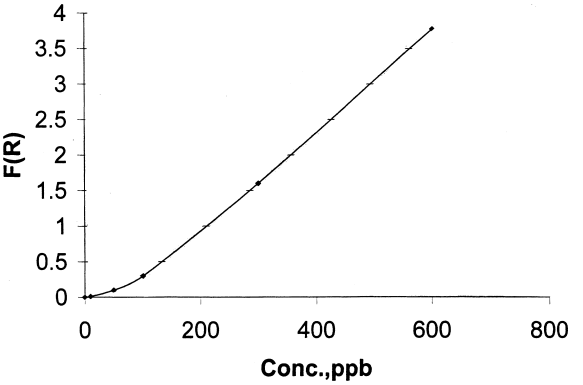

Fig. 2. Calibration plot for nickel(II) with nioxime.

Table 3
Effect of other metal ions on the determination of nickel(II)

Sample	R (%)	$F(R)$	Average $F(R)$
0.30 mg/l Ni^{2+}	19.98	1.602	
	20.18	1.579	1.587
	20.16	1.581	
0.30 mg/l Ni^{2+} +	21.07	1.478	
0.30 mg/l Co^{2+}	20.66	1.523	1.505
	20.76	1.512	
0.30 mg/l Ni^{2+} +	31.55	0.743	
0.30 mg/l Co^{2+}	30.33	0.800	0.781
	30.33	0.800	

Sample buffered at pH 6.0; diffuse reflectance (R) measured at 540 nm.

the average of three measurements which had a relative standard deviation of ±1% or less except for the two lowest points.

Cobalt(II) and copper(II) are among the metal ions most likely to interfere in the determination of very low concentrations of nickel(II). The data in Table 3 show excellent reproducibility in the measurement of 0.3 mg/l of nickel and only a 5.2% reduction of the Kubelka–Munk function when the sample also contains 0.3 mg/l of cobalt(II). However, the presence of 0.3 mg/l of copper(II) results in a 52% reduction of $F(R)$ and a shift in the diffuse reflectance spectrum to a more orange color (Fig. 3).

3.2.5. Iron(III)

An azo derivative of 8-hydroxyquinoline-5 sulfonic acid, known as SNAZOXS (chemical name: 7-(4-sulfo-1-naphthylazo)-8-hydroxyquinoline-5-sulfonic acid), is yellow but forms purple complexes with bismuth(III), iron(III), gallium(III) and indium(III) around pH 2–3 [16]. An Empore disk impregnated with SNAZOXS and a cationic surfactant (cetylpyridinium chloride or cetyltrimethylammonium chloride) can be used for the determination of iron(III) by C-SPE. It is necessary to use a cationic surfactant because the iron(III) complex has a net negative charge. A wavelength of 620 nm was selected for diffuse reflectance measurements, and a linear calibration plot was obtained for iron(III) between 1 and 10 mg/l.

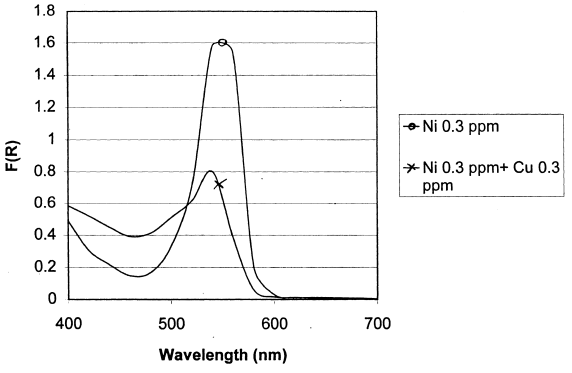

Fig. 3. Effect of copper(II) on the reflectance spectrum of nickel(II)–nioxime.

3.2.6. Chromium(VI)

Low concentrations of chromium(VI), which is much more toxic than chromium(III), must frequently be determined in aqueous samples. A strongly colored chelate of chromium(III) with diphenylcarbazone ($\varepsilon = 84\,000$) is formed by reduction of chromium(VI). However, the product sold as diphenylcarbazone is said to be grossly impure, and it forms colored complexes with several other metal ions [17].

Dichromate ions have a distinctive yellow-orange color with lambda maxima at 350 and 450 nm but the molar absorptivity is not very high. However, the concentration effect afforded by C-SPE permits the determination of chromium(VI) in the 0.2–2.2-mg/l concentration range using a 10-ml sample. A plot of the Kubelka–Munk function, $F(R)$, against the chromium(VI) concentration (C) in mg/l was linear between 0.2 and 2.2 mg/l and was expressed by the equation

$$F(R) = 0.208C - 0.027$$

The correlation coefficient was 0.9987. This plot was obtained with an Empore membrane disk impregnated with cetylpyridinium chloride. The positive charge on this surfactant strongly retains dichromate by ionic attraction. The aqueous sample was adjusted to approximately pH 6 by addition of HCl.

4. Conclusions

Analysts are accustomed to determining ionic analytes by ion chromatography or by various spec-

tral or electrical techniques. An initial preconcentration step is frequently needed to bring the analyte concentration into the required concentration range. A new approach, colorimetric solid-phase extraction, should be considered when a determination is needed for a single ionic analyte present in low mg/l or μg/l concentration. Analyses by C-SPE are very quick (1–2 min), require only the simplest equipment, and can be performed almost anywhere. A preconcentration step (~1000-fold in many cases) and measurement by diffuse reflectance spectroscopy are combined in a single analytical method.

Analysis by C-SPE should not be confused with older analytical techniques in which the concentration of an analyte is estimated by simply dipping a solid probe impregnated with a color-forming reagent into a liquid sample. The color intensity in this technique is influenced by the time of contact, the degree of agitation, and the partition coefficient, as well as the concentration of the analyte.

The analyte–reagent complex must be rapidly formed, have a reasonably high Kubelka–Munk function at the analytical wavelength, and be strongly retained by the extraction disk for a successful analysis to be performed by C-SPE. The method must also be selective for the target analyte and the accuracy not compromised by other ions likely to be present. Proper choice of the analyte complexing reagent, the sample pH, and the analytical wavelength are essential to achieve the required selectivity. Additional selectivity can sometimes be obtained by impregnation of the membrane disk with a cationic or anionic surfactant.

The most efficient membrane disks for C-SPE were found to contain cross-linked polystyrene-divinylbenzene- or reversed-phase silica particles of a fairly small diameter. Retention of analytes by complexation and extraction was found to be improved by swelling the membrane somewhat by addition of a non-ionic surfactant or a polar organic additive such as 1,2-decanediol. This appears to result in the formation of a phase within the membrane containing water as well as the organic additive.

The specific methods discussed in this paper are an indication that the scope of C-SPE is very broad. But combining a rapid SPE onto a membrane disk with some form of measurement of the analyte on the solid disk is a concept of extensive possibilities. The ultimate scope of C-SPE is limited only by the imagination and intuition of the analytical chemist.

Acknowledgements

Insightful discussions with Paul Mudgett, Jeff Rutz, and John Schultz are acknowledged. This work was supported by NASA under contract NAG91191, and by the Microanalytical Instrumentation Center at Iowa State University. The Ames Laboratory is operated for the US Department of Energy by Iowa State University under contract W-7405-eng-82.

References

[1] K. Matsuhisa, K. Ozeki, Analyst (1986) 685.
[2] H. Waki, J. Korkisch, Talanta 30 (1983) 95.
[3] O.P. Shvoeva, V.P. Dedkova, S.B. Savvin, J. Anal. Chem. 53 (1998) 1028.
[4] M. Lerchi, F. Orsini, Z. Cimerman, E. Pretsch, D.A. Chowdhury, S. Kamata, Anal. Chem. 68 (1996) 3210.
[5] V.M. Ivanov, O.V. Kuznetsova, O.V. Grineva, J. Anal. Chem. 54 (1999) 233.
[6] M.P. Arena, M.D. Porter, J.S. Fritz, Anal. Chem. 74 (2002) 185.
[7] M.P. Arena, M.D. Porter, J.S. Fritz, Anal. Chim. Acta 482 (2003) 197.
[8] G. Kortum, in: Reflectance Spectroscopy: Principles, Methods, Applications, Springer, New York, 1996, p. 106.
[9] W.W. Wendlandt, H.G. Hecht, in: Reflectance Spectroscopy, Interscience, New York, 1996, p. 23.
[10] J.S. Fritz, in: Analytical Solid-Phase Extraction, Wiley–VCH, New York, 1999, p. 73.
[11] K. Goto, N. Hata, Bunseki Kagaku 44 (1995) 169.
[12] E.B. Sandell, H. Onishi, in: Photometric Determination of Traces of Metals, Vol. 3, Part I, Wiley, New York, 1978, p. 513.
[13] J.S. Fritz, in: Analytical Solid-Phase Extraction, Wiley–VCH, New York, 1999, p. 150.
[14] J.N. King, J.S. Fritz, Anal. Chem. 57 (1985) 1016.
[15] J.M. Dale, C.V. Banks, in: I.M. Kolthoff, P.J. Elving (Eds.), Treatise on Analytical Chemistry, Vol. 2, Part II, Interscience, New York, 1962.
[16] G. Guerrin, M.V. Sheldon, C.N. Reilley, Chem. Anal. 49 (1960) 36.
[17] E.B. Sandell, H. Onishi, in: Photometric Determination of Traces of Metals, Vol. 3, Part I, Wiley, New York, 1978, p. 390.