Talanta 81 (2010) 1482–1488

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Quantification of trace metals in water using complexation and filter concentration

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ARTICLE INFO

Article history:
Received 18 October 2009
Received in revised form 16 February 2010
Accepted 22 February 2010
Available online 3 March 2010

Keywords:
Heavy metals
Water
Environmental analysis

ABSTRACT

Various metals undergo complexation with organic reagents, resulting in colored products. In practice, their molar absorptivities allow for quantification in the ppm range. However, a proper pre-concentration of the colored complex on paper filter lowers the quantification limit to the low ppb range. In this study, several pre-concentration techniques have been examined and compared: filtering the already complexed mixture, complexation on filter, and dipping of dye-covered filter in solution. The best quantification has been based on the ratio of filter reflectance at a certain wavelength to that at zero metal concentration. The studied complex formations (Ni ions with TAN and Cd ions with PAN) involve production of nanoparticle suspensions, which are associated with complicated kinetics. The kinetics of the complexation of Ni ions with TAN has been investigated and optimum timing could be found. Kinetic optimization in regard to some interferences has also been suggested.

1. Introduction

Heavy metals are natural components of the earth's crust. Although some heavy metals are essential in maintaining the metabolism of the human body, they are all hazardous at higher concentrations. Their concentration in drinking water should be kept in the low ppb range. In addition, metal ions interfere with some processes in modern semiconductor industries, where their concentration should be kept below ppb.

Conventional analytical methods (e.g., ICP-AES) are well defined for heavy metals analysis, but require expensive instrumentation and time consuming laboratory work. An alternative analytical approach is based on creating complexes of the heavy metals and detecting their optical properties. Such a method was recently proposed for heavy metals [1]. It was based on visual detection using dye-loaded membranes. Hg^{2+}, Ag^{+}, Cu^{2+}, Ni^{2+}, Pd^{2+}, Zn^{2+}, Co^{3+} and Fe^{2+} were detected using various aromatic dyes and the detection limits were in the sub-ppm range.Many metal complexes of azo compounds have been reported [2–5]. For example, 1-(2-thiazolylazo)-2-naphthol (TAN) was widely used as a spectrophotometric reagent for the determination of Pd^{2+}, Co^{2+}, $UO_2{}^{2+}$, Cu^{2+} and Zn^{2+} [6–9]. Due to its strong metal ion binding, it was also used for extraction and separation [10–15].

Lowering detection limits, without the use of complicated analytical instruments, should involve pre-concentration steps. Solid concentration media are preferred in this case, since they can be incorporated in test strips. However, production of such test-strips based on complexation with colorimetric and fluorometric reagents requires their fixation on solid substrates. Several attempts have been reported, using PVC based liquid membranes [16], covalent anchoring with cross-linked copolymers [17], layer-by-layer accumulation methods [18–19] and binding to solid membrane filters [20]. Test strips were successfully produced by filtrating organic reagents through cellulose ester membranes [20]. Drawbacks include complicated synthetic procedures, insufficient sensitivity, requirements for auxiliary additives, and difficulty in controlling the concentration of the reagent and its uniformity.

In this paper we tested the application of complexation reactions followed by pre-concentration of the products on various filters. Several operational modes were examined: complexation in solution, complexation during filtering and complexation during dipping. In all cases, quantification was based on measuring the reflectance at a defined wavelength. Since complexation and the associated reflectance are time dependent, we performed kinetic investigation, which has allowed for optimized timing for each complex, as well as handling some interferences.

2. Experimental

2.1. Materials

Two complexation agents were used: solid 1-(2-thiazolylazo)-2-naphthol (TAN) (from Sigma–Aldrich) and 1-(2-Pyridylazo)-2-naphthol (PAN) (from Mercury). The reagents were prepared

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doi:10.1016/j.talanta.2010.02.056

according to previously reported procedures (e.g., 20): they were dissolved in acetone and the solutions were injected to water solution under vigorous stirring. This results in suspensions of ca. 50–150 nm particles.

Buffer solutions were used for complexation: MES (pH 6.15) for Ni–TAN complexation and TRIS (pH 8.6) for Cd–PAN complexation (Sigma–Aldrich).

The metal ion solutions at the required concentrations were prepared from certified solutions (Sigma–Aldrich). The study of Fe^{3+} interference was performed using a 100 ppm acidified stock solution of Ferriammoniumsulfat $[NH_4Fe(SO_4)_2]$.

The following filters were used in the reagents deposition experiments, in the complex filtration measurements and in filter dipping tests: paper filter Whatman-5, 2.5 μm pore size, 54 mm O.D. and Whatman-3, 6 μm pore size, 54 mm. O.D. Mixed Cellulose Ester (MCE) Membrane Filter 0.8 μm pore size, 37 mm O.D., GN-4 Metrical® (Pall Corp Filters, Michigan, USA).

2.2. Spectral absorption measurements

The absorption spectra were measured using a diode array spectrometer (Hewlett Packard, HP-8453).

2.3. Spectral reflection measurements

Reflection spectra from filter surfaces were measured using two spectrometers:

(1) Aminco-Bowman Series II luminescent spectrometer, Thermo Electron Corp., Madison, WI, equipped with pulsed Xe lamp. It uses two monochromators for scanning the excitation and emission wavelengths at 1 nm resolution. It was operated in its synchronous mode with no difference between the excitation and emission wavelengths.
(2) Double beam UV–VIS spectrophotometer Evolution 300 (Thermo Fisher Scientific Inc. USA) equipped with Xe flash-lamp, 0.5 nm spectral resolutions. Surface reflections were collected with a diffuse reflectance accessory (DRA-EV-300).

2.4. Particle characterization

Imaging of the dye and complex particulates was performed using Transmittance Electron Microscope (TEM) FEI Tecnai G^2 T20 S-Twin.

Particle size measurements were performed using a zeta potential-particle seizer, Nicomp^{TM}380 ZLS (Particle Sizing System, Santa Barbara, CA).

3. Results and discussion

3.1. Characterization of complex particulates

The proposed method is based on the complexation of metal ions with organic dyes. Actually, some of the dyes are not soluble in water. They are introduced as a suspension of nanoparticles or nanofibers, with a characteristic diameter of 100 nm. This suspension is formed by injecting a solution of the dye in an organic solvent (acetone) into the water, under vigorous stirring.

The size distribution of the dye nanoparticles might depend on the details of the preparation procedure and might also be affected by matrix compounds and impurities. In turn, the size distribution of the dye particulates should affect the kinetic behavior of the complexation reaction. In this study we investigate the kinetics and analyses obtained using nanoparticles prepared by the above mentioned procedure and characterized in the following.

3.1.1. TEM analysis

Characteristic TEM pictures of PAN and TAN particles are provided in Fig. 1. Clearly, PAN particles are smaller than the TAN particles, and so are their corresponding complexes with heavy metals. This can explain the much faster reaction rate of PAN with Cd ions, compared to the reaction rate of TAN with Ni ions. Moreover, the Cd-PAN complex particles are more porous than those of the Ni–TAN.

The mechanism of the complexation of the metal ions with the nano-dyes is not yet known and not understood. Most probably, the metal ions react with the dye molecules on the surface of the nanoparticles. The resulted complex might get dissolved in water, or might remain adsorbed to the particle. The corresponding partition coefficient probably depends on the chemical nature of the reagents, on pH, as well as on the particle size of the dye. They might also form separate particulates.

Moreover, it could be that the complexation mechanism and its chemical products depend on the concentration of the metal ions. In the general case, the reaction rate depends also on the number concentration of the particulates, since at too low concentration the reaction is limited by diffusion.

3.1.2. Size distribution of Cd–PAN and Ni–TAN particulates

The size distribution of both Cd–PAN and Ni–TAN particulates is bimodal: the location of the peaks and their width are affected by metal concentration: when Cd ion concentration is increased, the location of the peak corresponding to small particles is only slightly affected. However, the location of the large-particle peak is much more affected by increasing the metal concentration: it moves from 1400 nm to 100 nm, and its width decreases from 200 nm to 20 nm.

In contrast to the Cd-PAN case, when the concentration of Ni ions is increased, the location of the peak of the large Ni–TAN particles moves to larger sizes, and its width increases. It moves from 600 nm to 2000 nm, and its width at half-height increases from 250 nm to 600 nm. Clearly, the dependence of the size distribution upon metal concentration is different in the two studied complexes. These results indicate possible dependence of the complexation and/or aggregation mechanism upon metal concentration.

3.2. Complexation kinetics

In order to find the optimal time needed for successful quantification, we have investigated the kinetics of the complexation of the dyes with some metal ions. In all cases, we applied rather high dye concentrations, such that the characteristic distance between the nanoparticles is of the order of a few microns. This ensures that the reaction rate is not diffusion limited. The reaction of Cd with PAN nanoparticles is fast, of the order of 30 s. However, the reaction of TAN with Ni ions is much slower and allows for easy monitoring.

A 100 μl of TAN solution in acetone was injected into 10 ml solution of x ppm Ni ions in buffered water (MES, pH = 6.15), where x = 0, 0.25, 0.5, 1.0, and 1.5 ppm. The injection was carried out under vigorous stirring and the final TAN concentration was 1 ppm. The absorption spectra of the mixture were measured as a function of time.

Also when no Ni ions are present in the solution the absorption spectra change as a function of time. Generally, one can observe four spectral peaks: 330 nm, 500 nm, 560 nm and 620 nm. We will focus on the most distinct peaks at 500 nm and 620 nm. The former is traditionally related to TAN. These results indicate a considerable change that takes place in the solution, which is independent on the presence of Ni ions and which last ca. 4 min.

Checking the spectrum of 1 ppm TAN in acetone indicates that the peak and the spectral feature above 600 nm are completely missing in this case. The features in this spectral range are totally attributed to the injection into water: first, a change in the pro-

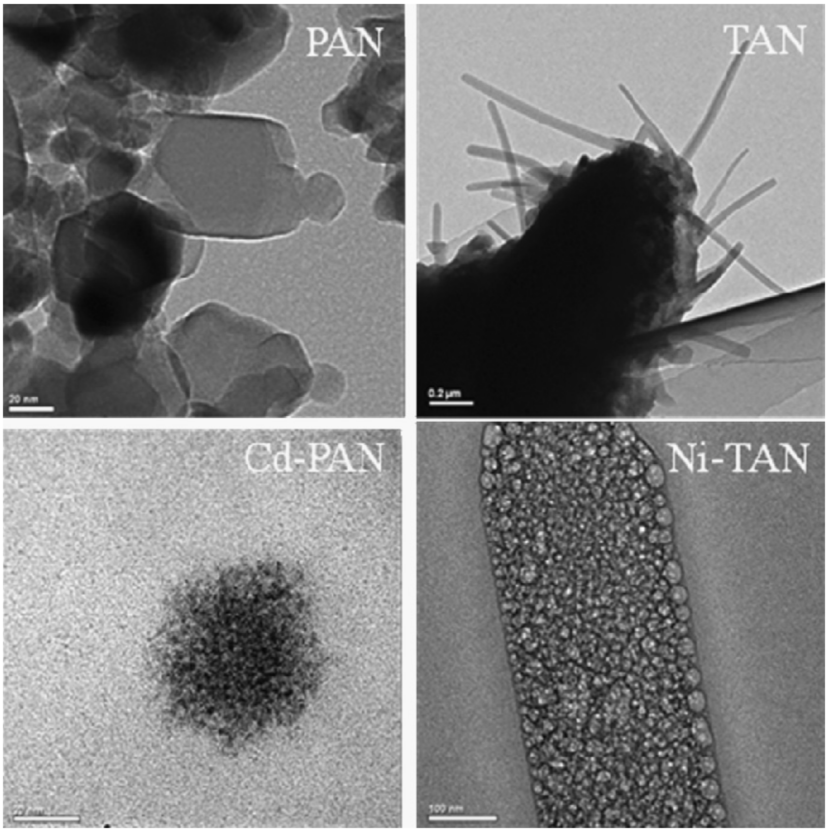

Fig. 1. TEM images of dye and complex particulates. Top-left: PAN, scale = 20 nm, top-right: TAN, scale = 200 nm, bottom left: Cd–PAN, scale = 20 nm, bottom-right: Ni–TAN, scale = 100 nm.

tonation state takes place, as a result of exposing the dye to the buffered pH. In addition, the formation of TAN nanoparticles, which affects the inter-molecular interactions, starts. With time, coagulation of dye nanoparticles, dissolution of small particles and re-crystallization associated with crystal growing may also take place. The long time behavior may indicate a slow decomposition, or coagulation/crystal grow, which results in precipitation of large particulates (thus eliminating their spectral contribution).

The kinetics change when Ni ions are present: an exponential decay was observed at 500 nm, at two Ni^{2+} concentrations (0.25 ppm and 0.5 ppm). Single exponential decay fitting shows characteristic decay times of 7 min and 10 min, correspondingly. However, single exponential fitting is not sufficient, and much better fittings are obtained using a sum of two exponentials. In this case, the characteristic times for 0.25 ppm Ni^{2+} were 4 min and 28 min and for 0.5 ppm Ni^{2+} they were 4.6 min and 48 min. This means that the process controlling the long time decay is mainly affected by the Ni ion concentration. These results make sense, in view if the fast decay with no Ni ions, which is also of the order of 4 min.

At the same time, the 620-nm peak rapidly increases, reaches a maximum and then slowly decreases. Note that this wavelength has traditionally been attributed to the $Ni(TAN)_2$ complex. Without Ni ions, the maximum is reached in ca. 4 min, however, in the presence of Ni ions the maxima are reached at about 13 min (for both concentrations). However, the maximum reached at the higher Ni ion concentration exceeds that of the lower concentration. Clearly, this maximum can be utilized for Ni ion quantification. After the maximum is reached, a relatively slow decay starts: 10% decay in an hour at the high Ni ion concentration and 20% decay in an hour at the lower Ni ion concentration. These results indicate that accurate analysis based of spectral measurements in this system must be carried out at precise timing.

The spectra in the vicinity of the optimum timing (obtained from the kinetic analysis), include contribution of all peaks, since the decay of the 500-nm peak has a time constant similar to that if the increase of the 620-nm peak. The spectra at this time were measured for complexation of 2.6 ppm TAN suspension with three concentrations of Ni ions (Fig. 2). All relevant peaks are clearly distinct at this time: the two peaks that are usually related to the complex, at 560 nm and 620 nm, clearly increase with Ni ion concentration, while the peaks related to the TAN (especially at 500 nm) decrease with concentration.

The spectra measured at a long time of 300 min, are also of interest. The results for various Ni ion concentrations are shown in Fig. 3. It can be seen that also at long times, the peaks related to $Ni(TAN)_2$

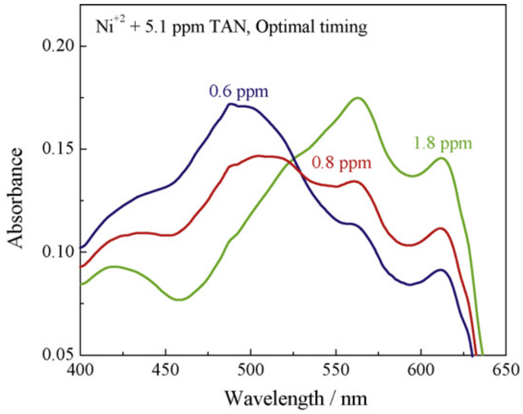

Fig. 2. Absorbance spectra of Ni–TAN complexation at optimum timing, for various Ni^{2+} concentrations.

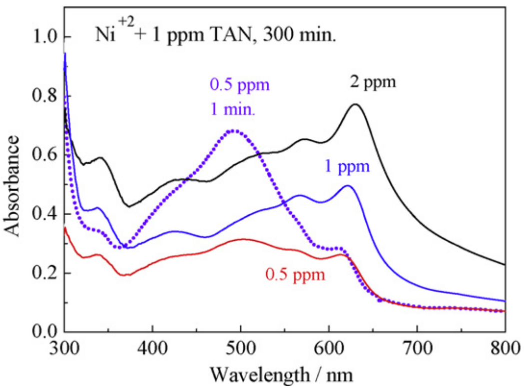

Fig. 3. Absorbance spectra of Ni–TAN complexation after 5 h, for various Ni^{2+} concentrations.

complex increase with Ni ion concentration. At long times, these peaks are better resolved, since the large peak at 500 nm diminishes.

Explanation of the kinetic data requires further investigation, since the kinetic scheme is a complicated one. Based on the kinetics at zero Ni ion concentration, we believe that several processes take place in parallel with the conversion of TAN to TAN–Ni complex. Note that these processes have comparable time constants. Nevertheless, measuring at the optimal timing as described in the above, definitely improves the analytical performance. In view of the described kinetics, it is clear that the previous procedure, which prescribed "waiting sometime before performing the measurement", is responsible to serious repeatability problems experienced in this method.

3.3. Filter concentration

Previous reports indicates that the complexation of metal ions results in a color change, which can be utilized for estimating concentrations. When concerning with metal ions in water, the detection limits were usually in the ppm range. Several factors prevent further lowering of the detection limits. First, the molar absorptivities of the complexes are not very high. In addition, there are other obstacles as well: the organic dyes TAN and PAN do not dissolve in water and form nanoparticle suspensions. The particulate size distribution is very sensitive to various experimental parameters. They partially scatter light (according to their size) and affect the absorption measurements. Moreover, the complexation kinetics is often such that precise timing is needed (sometimes on the order of seconds).

Therefore, lowering the detection limits requires a pre-concentration step. The most promising concentration method has recently been suggested and tested for detection of Zn ions using a PAN coated membrane [20]. The dye nanoparticles were deposited on a membrane, which, in turn, was dipped into the aqueous analyte for 15 min. The Detection limits for visual inspection were 65 ppb. Filtration through the same membrane and measuring the spectral reflection resulted in a calibration plot up to 1300 ppb, which was linear in the 0–100 ppb range.

We have examined three modes of concentrating the complex, which provide quantitative results. They were applied to detection of Ni and Cd ions in the low ppb range, using TAN and PAN dyes, correspondingly. Note that these are the first quantitative results on Cd ion analysis using this method. These modes are summarized in the following:

(a) Pre-complexation in suspension followed by pre-concentration on filter.
(b) Collection of nano-dyes on filter followed by complexation during filtering.
(c) Collection of nano-dyes on filter followed by complexation during dipping.

In all methods, the color change is produced on the filter and monitored using reflection spectroscopy, as explained in the experimental session. These three concentration methods and some representative results are described in the following.

3.3.1. Pre-complexation in suspension followed by on-filter pre-concentration

For simplicity, this method will be thereafter named "complexation-in-suspension". In this method, the dye is firstly dissolved in acetone (1 g/L). Then, 450 μl of this solution is injected into 1 L of the properly buffered examined water, under vigorous stirring. This starts a simultaneous formation of nanoparticle suspension of the dye and its complexation reaction with the metal ions. Then, after a definite time needed for reaching the maximal signal (ca. 15 min for Ni–TAN), the mixture was filtered and the reflection spectrum of the filter was measured. The ratio of the actual reflectance spectrum to that obtained in the same procedure but using pure water, is presented and used for calibration.

The main advantage of this method is that it allows for precise timing for optimal developing of the colored complex. The drawback is that analysis requires following the above chemical procedure, which cannot be considered as a simple on-line test.

For example, the method was applied to Ni ion detection in the concentration range of 5–20 ppb. Complexation was carried out with 0.45 ppm TAN, buffered with MES at pH 6.15. The wavelength which is mostly indicative of the complex formation is 620 nm. This is in agreement with previous reports [20]. The calibration plot based on the reflectance ratio at this wavelength was linear in this concentration range. Note that as the absorbance increases at a given wavelength, the reflection decreases.

Another example for the method of complexation-in-suspension is the detection of Cd ions using PAN dye. Complexation was carried out with 0.52 ppm PAN, buffered with TRIS at pH 8.6. As in the previous method, the dye is first dissolved in acetone (1 g/L). 520 μl of this solution is injected into 1 L of the properly buffered examined water, under vigorous stirring. The ratio of the resulting reflectance spectra were plotted and the wavelength which was mostly indicative of the complex formation was 450 nm. Linear calibration plot based on the reflectance ratio at this wavelength was constructed and resulted in detection limit in the low ppb range.

3.3.2. Comparing various filters

The results of the on-filter pre-concentration depend of the properties of the filter used. The differences are in the pore size, which affects the quantity of complex retained, the 3D structure, which affects the quantity of material left on the surface and available for reflectance measurement, and material affinity, which determines the nature of adhesion of the complex to the filter.

When concerning with spectral measurements and utilizing a diffuse reflectance accessory, the pore size is the most relevant parameter (smaller is the better). Nevertheless, somewhat better calibration plots were always obtained using the membrane filter. For example, the calibration plot for Ni ions, using paper filter results in LOD of 1.8 ppb, while that obtained using the membrane filter (Figs. 4 and 5) results in LOD of 1.2 ppb.

However, when concerning with visual color detection, the results obtained using the membrane filter were better that those obtained with paper filters (of the same pore size). See, for example, photos of paper filters corresponding to measurement of a series of Ni ion concentrations (in the low ppb range), Fig. 6. These photos

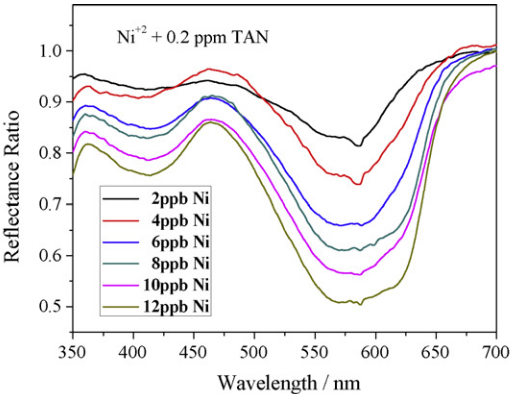

Fig. 4. Spectra of cellulose membrane filter reflection ratio for a series of Ni^{2+} concentrations reacting with 0.2 ppm TAN.

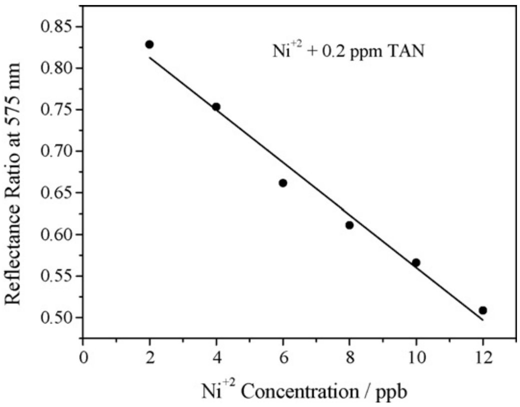

Fig. 5. Calibration plot for Ni ions based on cellulose membrane filter reflection ratio at 575 nm, measured with the spectrometer equipped with the diffuse reflectance accessory.

should be compared to those presented in Fig. 7, which correspond to the same concentrations, but using the membrane filters.

3.3.3. Collection of nano-dyes on filter followed by complexation during filtering

For simplicity, this method will be thereafter named “complexation-on-filter”. In this method the dye is dissolved in acetone (1 g/L). 450 μL of this solution is injected into 50 ml of properly buffered pure water, under vigorous stirring. This starts the formation of nanoparticle suspension of the dye. The suspension is filtered, such that most of the dye particulates are found on the filter surface. 300 ml of the examined water is filtered through the dye-covered filter, at a rate of ca. 3.6 ml s^{-1}. The filter

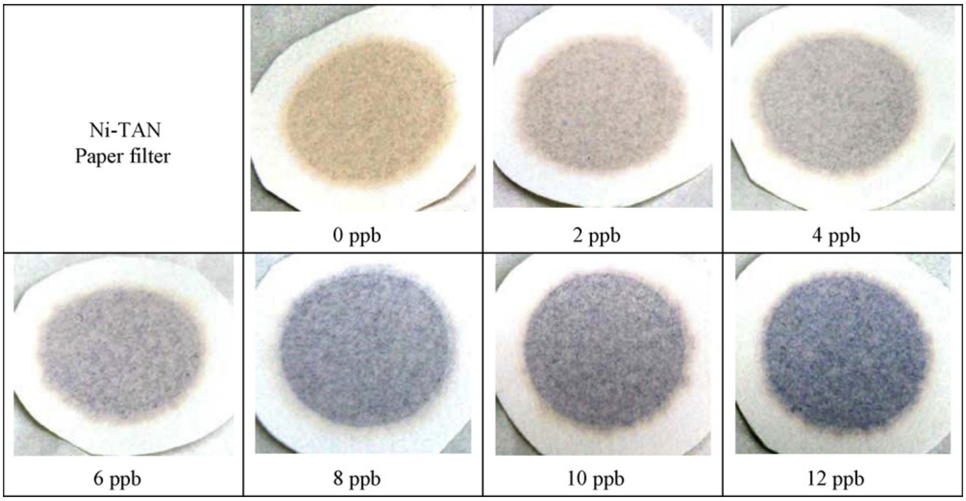

Fig. 6. Photos of Ni–TAN on Whatman paper filters, obtained at a series of Ni ion concentrations.

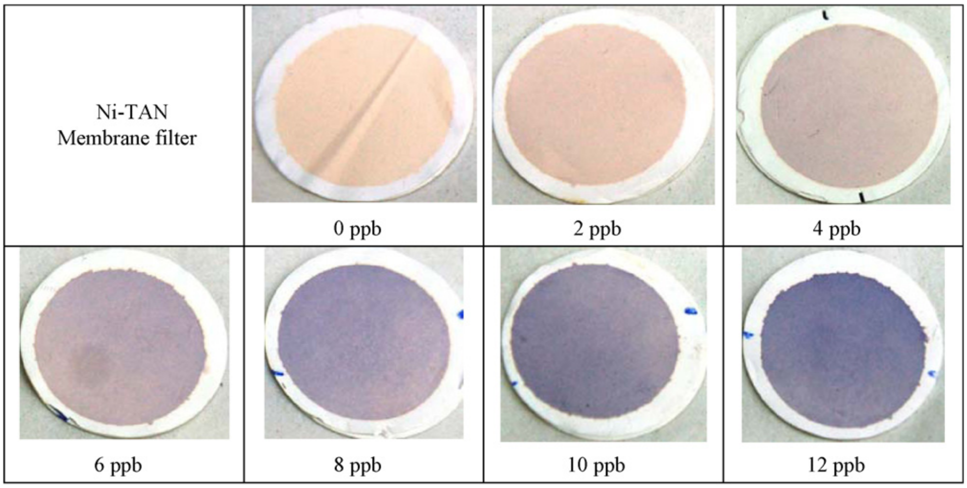

Fig. 7. Photos of Ni–TAN on membrane filters, obtained at a series of Ni ion concentrations.

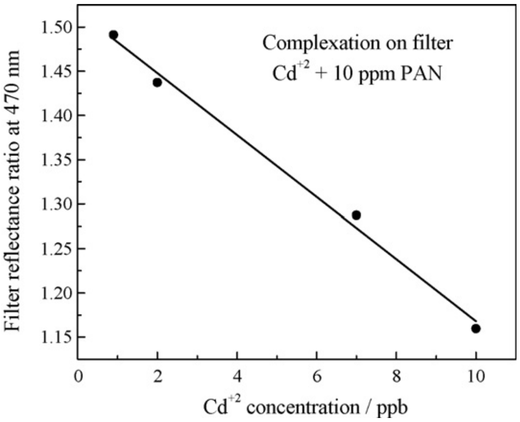

Fig. 8. Calibration plot for Cd ions based on filter reflection ratio at 470 nm.

is air-dried (while completing the complexation process on the filter). The reflection spectra are then measured. The ratio of the actual reflectance spectrum to that obtained in the same procedure but using pure water, is presented and used for calibration.

The main advantage of this method is its simplicity. The dye-covered filter can be prepared in advance, and analysis requires only filtering of the examined water and inspecting the filter. The main drawback is that the results are sensitive to the filtration rate. Filtering of too much water might partially flush the dye/complex and cause errors. Moreover, the stability of such prepared filters has not been studied.

For example, the method was applied to Ni ion detection in the concentration range of 0.9–6 ppb. Complexation was carried out with 9 ppm TAN, buffered with MES at pH 6.15. The wavelength which is mostly indicative of the complex formation is 620 nm. The calibration plot based on the reflectance ratio at this wavelength was linear in this concentration range.

Another example of complexation-on-filter is the detection of Cd ions using PAN dye. Complexation was carried out with 10 ppm PAN, buffered with TRIS at pH 8.6. The wavelength which is mostly indicative of the complex formation is 470 nm. The calibration plot based on the reflectance ratio at this wavelength is shown in Fig. 8. The results indicate sensitivity in the low ppb range.

3.3.4. Collection of nano-dyes on filter followed by complexation during dipping

For simplicity, this method will be thereafter named “filter dipping”. In this method the dye is dissolved in acetone (1 g/L). 0.4 ml of this solution is injected into 50 ml of pure water, under vigorous stirring. This starts the formation of nanoparticle suspension of the dye. The suspension is filtered, at a rate of ca. 1.5 ml s^{-1}, such that most of the dye particulates are bound to the filter. For analysis, the filter is dipped in the examined water for 15 min. This initiates the complexation process on the filter. The reflection spectra are then measured. The ratio of the actual reflectance spectrum to that obtained in the same procedure but using pure water, is presented and used for calibration.

The main advantage of this method is that its application is simple and does not require any procedure but dipping the filter into the water for a definite time. The drawback is that it requires stirring (otherwise diffusion sampling takes too long) and the results depend on the actual stirring performed.

For example, the method was applied to Ni ion detection in the concentration range of 0.9–6 ppb. The wavelength which is mostly indicative of the complex formation is 620 nm. The calibration plot based on the reflectance ratio at this wavelength was linear in this concentration range.

3.4. Interferences

The complexation of TAN and PAN with the analyte might be interfered by the presence of other compounds in the solution. The complexation mechanism is a complicated one and it might be affected by various factors. Therefore, a comprehensive investigation is needed. We studied, as an example, the effect of Fe ions upon the complexation of Ni–TAN and Cd–PAN and the resulting analyses.

We tested rather high concentrations of the interfering compound (Fe ions): up to 500 ppb. In all cases, linear calibration plots were obtained. For example, Cd ions were detected in the range 2–12 ppb, using complexation with PAN in the presence of interfering Fe ion at a concentration of 50 ppb. The detection of Ni ions in the presence of Al ions was also accomplished. However, the problem was that the calibration plots were somewhat dependent on the concentration of the interfering ion.

In order to resolve this issue, we studied the effect of the interfering compound upon the kinetics of the complex formation. The absorbance at two wavelengths was measured as a function of time, for Ni–PAN complexation (without interferences) and for the complexation in the presence of Fe ions at 250 ppb and 500 ppb.

The absorbance at 500 nm wavelength indicates that the interfering ion modifies both the kinetic constants and the asymptotic value (at long times). The kinetic constant of the absorbance decay is considerable changed by both 250 ppb and 500 ppb of Fe ions, however, the asymptotic values are modified by less than 20%. It indicates that when measurements are carried out at 500 nm wavelength, a long delay might compensate for some interferences.

The interference at 610 nm wavelength is different. In this case the interference is time dependent and it come out that at a delay time of ca. 15 min the effect diminishes. This time is close to the optimum analysis time (as previously described), so in this case, measuring at 610 nm might provide accurate results, eliminating the interference effect.

In addition to the above, one might expect interfering effects of non-complexable metal ions and of soluble ligands in the sample. Such effects have not been studied yet and their understanding might contribute to further lowering the limits of detection.

3.5. Reproducibility

The success of the analytical method depends on the reproducibility of the nanoparticle production. This was a known issue in previous applications of production of such nanoparticles for analytical use. This problem is now clear in terms of the time dependent processes described in the above. We have tested the reproducibility of the kinetics, in independent measurements, and found out that it is of the order of 10%. Comparison of independent TEM images of the complex nanoparticles indicates that when using the same stock of dyes, the resulted size distribution and shape of the nanoparticles look very similar. Also the reproducibility of filter collection and the resulted reflectance measurement has been tested (for a constant concentration). It varies with wavelength and found to be less than 5% at the relevant wavelengths (and up to 15% at other wavelengths).

This study has been conducted using a single stock of dyes, which resulted in well characterized dye nanoparticles and complexes. We cannot exclude the possibility that dyes produced in different batches might result in different size distribution of nanoparticles. This could affect the analytical results. However, note that we first dissolve the dye in an organic solvent, so only persistent fluctuating impurities might influence the nanoparticle generation. Nevertheless, this effect of impurities has not been studied yet.

It has been found that the surface reflectance depends on the filter type, so good reproducibility can only be expected within the same type.

4. Conclusions

Pre-concentration of the complexation products on filters allows for increased sensitivity to metal ion detection. However, since the organic complexant is not soluble in water, the complexation is performed in suspension of nanoparticles. Kinetic investigation of the complexation has revealed that several parallel processes take place, in addition to the main reaction. An optimal timing was found to provide best results, however, this timing depends on several experimental parameters needed to be under control. Kinetic size distributions of the involved nanoparticulates have been reported for the first time. This information reveals the complexity of the reactions and is important for further optimization and reducing the detection limits. The kinetic data has been found useful for improving reproducibility, since so far it was not know that precise timing is crucial in such analyses.

Several modes of filter concentration have been examined and compared: depositing the complexant of a filter and dipping it into the water is the simplest procedure, but it suffers from several drawbacks. Performing the complexation in a vessel and filtering the products for their concentration provides good results, but lacks the simplicity. Depositing the complexant particulates on a filer and filtering the tested solution for performing the complexation on the filter provides good calibration plots, but requires individual optimization of the procedure and so far is not effective in the low ppb range. It seems that so far the most practical method, which works well in low concentrations, is the complexation in solution, followed by filtering. However, it is hoped that full understanding of the complexation mechanism and of the interactions of the complex nanoparticles, might result in improving the much simpler method of complexation during filtering.

In the current work the detected concentrations were in the low ppb range, but it seems that the ultimate detection limits can further be improved below ppb. The effect of additional non-complexable metal ions, and the effect of soluble ligands is still to be studied. This study should be considered as a progress towards the development of a new fast and simple analytical technique for heavy metals in water, however, it is clear that additional insight into the complicated processes associated with reaction of nanoparticles, is still required.

Acknowledgments

This project has been supported by the Israel Council for High Education – the Planning & Budgeting Committee and by the James Frank program in laser matter interaction. VB thanks the ministry of immigrant absorption for financial support (KAMEA Program).

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