Application of *Dipon*, (1,4,8,11-Tetraazacyclotetradecane-4,11-bis(methylphosphonic acid) as Selective Complexing Agent for Determination of Copper(II)

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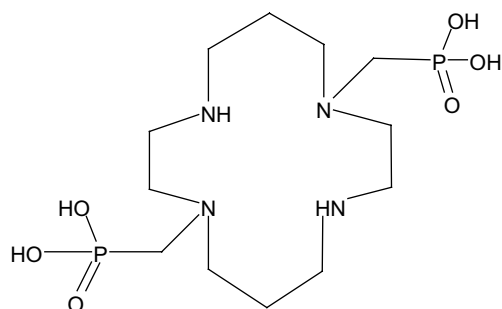
Abstract

A new macrocyclic ligand, 1,4,8,11-tetraazacyclotetradecane-1,8-bis(methylphosphonic acid) (*dipon*), is selective complexing agent for copper(II) over other transition metal ions. The ligand was tested for analytical applications of copper(II) determination. Spectrophotometric determination under optimal experimental conditions ($-\log [H^+] = 5.5$, $c_L \approx 5 \times 10^{-4}$ mol L^{-1}, $\lambda = 310$ nm) is valid in dynamic range $(5–200) \times 10^{-6}$ mol L^{-1} with detection limit 2.2×10^{-6} mol L^{-1}, i.e. 0.14 μg ml^{-1}. Volumetric determination of copper(II) with standardized *dipon* solution was used for copper(II) determination at micromolar concentration level without any necessity to sequester interfering metal ions. A sharp end point of titration was detected by UV/VIS spectrophotometry. Both methods were tested on artificial and real samples (spiked mineral water, alloys) and gave satisfactory results without any systematic error. The advantage of both methods is their simplicity, rapidity and no sensitivity to the presence of other metal ions.

Introduction

Complexometric titrations are widely applied mainly for the determination of transition metal ions [1, 2], as ethylenediamine-*N,N,N′,N′*-tetraacetic acid (*edta*) is widely used as a titration agent [1, 2]. Other aminopolycarboxylate ligands, such as nitrilotriacetic (*nta*), *trans*-diaminocyclohexane-*N,N,N′,N′*-tetraacetic (*dcta*) and diethylenetriamin-*N,N,N′,N′′,N′′*-pentaacetic (*dtpa*) acids, are applied for volumetric determination of a variety of transition metal ions [1]. Therefore, it is not possible to titrate metal ions with those ligands selectively, e.g. to determine copper(II) in presence of other common metal ions (zinc(II), nickel(II), iron(II,III), lead(II), etc.) [1]. In order to increase selectivity of titration of copper(II), some more selective aminopolycarboxylate ligands, e.g. ethylenediamine-*N,N,N′,N′*-tetrapropionic acid (*edtp*), bis(aminoethyl)glycolether-*N,N,N′,N′*-tetraacetic acid (*egta*) and *N,N,N′,N′*-ethylenediamine-tetrakis(methylphosphonic acid) (*edtmp*), have been employed [1, 3]. Another possibility is use of various sequestering agents in order to eliminate the

effect of interfering ions. For the determination of copper(II) in the presence of other transition metal ions, thiourea [4], thioglycolic and β-mercaptopropionic acids [5], DL-cystein [6], 2-mercaptoethanol [7], 1,10-phenanthroline [8] or 2,2′-bipyridyl [9] has been used as masking agents. Also a ternary masking mixture comprising a main complexing agent (thiourea), a reducing agent (ascorbic acid) and an auxiliary complexing agent (thiosemicarbazide or a small amount of 1,10-phenanthroline or 2,2′-bipyridyl) has been applied for highly selective complexometric volumetric determination of copper [10]. This procedure is based on indirect determination when the content of copper(II) is determined from volume difference without and with addition of a masking agent [1]. The composition of the solution of masking agents is strongly dependent on the composition of the sample. In alkaline pH region, polyamines are more selective chelating agents than polyaminocarboxylates, as it follows from Irwing–Williams order [11]. Applications of some aliphatic polyamines, e.g. triethylenetetramine (*trien*) or tetraethylenepentamine (*tetren*), as titration agents for copper(II) determination in presence of other metal ions were described in the literature both in aqueous and nonaqueous media [12–

Scheme 1. Formula of the ligand 1,4,8,11-tetraazacyclotetradecane-1,8-bis(methylphosphonic acid), *dipon*.

14]. For example, *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-ethylenediamine (*tpen*) was proposed as a complexing agent for volumetric determination of metal ions (copper(II), nickel(II), zinc(II), cadmium(II) and lead(II)), a masking agent in acidic medium and a metal buffer [15]. However, macrocyclic ligands are utilized widely in analytical chemistry [16], only a rare application of macrocyclic ligands for volumetric metal determination can be found in the literature [17]. The use of mixed nitrogen-sulfur and tetraaza macrocycles with *vic*-dioxime units has been studied for volumetric determination of nickel(II), copper(II) and cobalt(II) with potentiometric end-point detection [17].

The macrocyclic ligand, 1,4,8,11-tetraazacyclotetradecane-1,8-bis(methylphosphonic acid) (*dipon*, Scheme 1) [18], demonstrates high thermodynamic and kinetic selectivity to copper(II) over other common transition metal ions [19–21, J. Kotek *et al.*, unpublished results]. Therefore, in this short contribution, possible application of this ligand for selective spectrophotometric and volumetric determinations of copper(II) in presence of other metal ions was investigated.

Experimental

The *dipon* ligand was synthesized by a published method [18]. The CuCl$_2 \cdot$2H$_2$O (p.a.) was obtained from Fluka (Switzerland) and was standardized by complexometric titration according to recommended procedure [1, 2]. The other chemicals (mostly other metal chlorides) were purchased from Lachema (Czech Republic), Fluka (Switzerland) and Merck (Germany) and were used as obtained. The prepared solutions were also standardized according to recommended procedures [1, 2].

The alloys (reference materials) were dissolved in ternary mixture nitric acid–hydrochloric acids–water (v/v%: HNO$_3$ 25, HCl 42, water 33) and heated up to evaporate nitric acid. The final $-\log [\mathrm{H}^+] = 5.5$ of solutions used for the titration was adjusted by addition of ammonia and acetic acid. Copper content in alloys was declared while the percent content of other elements was determined by ICP AES (Jobin-Yvon 170 Ultra-

trace, France). For copper(II) determination in water, artificial samples were prepared. Mineral water "*Magnesia*" (Karlovy Vary, Czech Republic; composition in mg L^{-1}: Na$^+$ 5.4, Mg^{2+} 234, Ca^{2+} 37.7, Mn^{2+} 0.2, F$^-$ 0.2, Cl$^-$ 5.34, SO$_4^{2-}$ 29.9, HCO$_3^-$ 1403.3, total mineralization 1870 mg L^{-1}) was spiked with known addition of copper standard solution in order to achieve final concentration 1.00×10^{-4} mol L^{-1}. Mineral water "*Poděbradka*" (Poděbrady, Czech Republic; composition in mg L^{-1}: Na$^+$ 354.6, K$^+$ 49.3, Mg^{2+} 47.5, Ca^{2+} 144, F$^-$ 1.3, Cl$^-$ 373.3, SO$_4^{2-}$ 76.8, HCO$_3^-$ 955.5, 2027 mg L^{-1}) was also spiked with copper(II) in order to achieve final concentration 2.00×10^{-4} mol L^{-1}.

The volumetric determination was done at room temperature and $-\log [\mathrm{H}^+] = 5.5$ (acetate buffer concentration 0.1 mol L^{-1}). Unknown amount of copper(II) in the solution was usually titrated by standardized *dipon* solution ($c_{\mathrm{dipon}} = 4.587 \times 10^{-3}$ mol L^{-1}). The solution was pumped by peristaltic pump through flow cell in which the spectrum of titrated solution was recorded by PYE UNICAM UV2 spectrophotometer (PYE UNICAM, United Kingdom). Measured absorbance was corrected for the dilution of the solution and then the end-point was estimated from the break point of the titration curve monitored spectrophotometrically at selected wavelength. Each titration was repeated at least three times and average volume was used for the calculation of copper content in the samples. The spectrophotometric determination was carried out under the same experimental conditions as the volumetric and concentration of *dipon* was 4.587×10^{-4} mol L^{-1}.

Results and discussion

Spectrophotometry

The *dipon* ligand forms the [M(H$_x$L)]$^{2-x}$ complexes ($x = 0$–2) with common metal ions (Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Pb(II), Mg(II), Ca(II) [19–21, J. Kotek *et al.*, unpublished results]. The copper(II) complex species are much more stable than complex species formed with zinc(II), cadmium(II), lead(II), cobalt(II), nickel(II), magnesium(II), calcium(II), strontium(II) and barium(II) ions in aqueous solution [19–21, J. Kotek *et al.*, unpublished results]. As can be seen from Figure 1, the metal complex species are formed quantitatively (log $\beta_{\mathrm{cond}} \approx 8$) at $-\log [\mathrm{H}^+] > 5$ (Cu – 5.0, Ni – 6.5, Zn, Co – 7.5, Cd – 8.5) neglecting the hydrolysis of metal ions in the solution in cases when the ligand is in an excess with respect to the metal ion. Complexing thermodynamic selectivity of the *dipon* ligand to copper(II) with respect to most of metal ions is practically constant in broad $-\log [\mathrm{H}^+]$ region (Figure 1). The selectivity of *dipon* to copper(II) is lowest for divalent metal ions nickel(II) (about 3 order of magnitude) and zinc(II) (about five orders of magnitude) (Figure 1). The kinetic selectivity of *dipon* to copper(II) in comparison
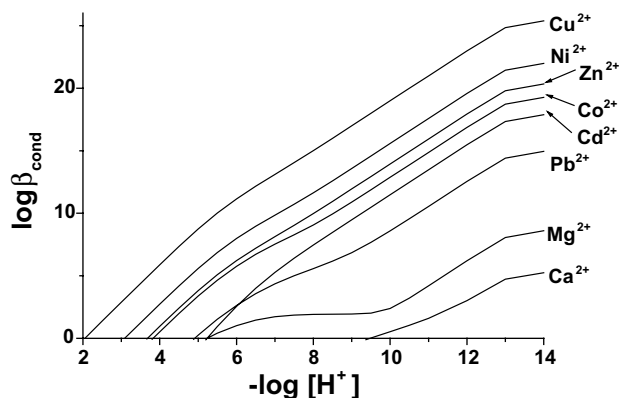
Figure 1. Calculated conditional constants of *dipon* complexes with metal ions as a function of $-\log [H^+]$ for experimental conditions ($I = 0.1$ mol L^{-1}, $t = 25$ °C). Protonation and stability constants were taken from [18–22].

to divalent metal ions is also 2–3 orders higher (data not shown) in the region of $-\log [H^+] = 0$–5.5 [19–21, J. Kotek *et al.*, unpublished results]. This solution acidity ($-\log [H^+] > 5$) is suitable from the practical point of view, as the reaction applied in analytical chemistry should be as fast as possible. The reaction of copper(II) with *dipon* (at $-\log [H^+] = 5.5$) takes milliseconds while the complete reaction with zinc(II) needs minutes [J. Kotek *et al.*, unpublished results]. The upper value of $-\log [H^+]$ ($-\log [H^+] < 7$) is limited by copper(II) hydrolysis in aqueous solution and by the loose of kinetic selectivity of *dipon* for copper(II), therefore, the value $-\log [H^+] = 5.5$ was chosen for spectrophotometric determination of copper(II).

The calibration curve for spectrophotometric determination of copper(II) by means of *dipon* ligand is displayed in Figure 2a. The plot is linear in dynamic range $(5$–$200) \times 10^{-6}$ mol L^{-1} and the slope is equal to (4460 ± 30) 1 mol^{-1} cm^{-1} which corresponds, under

given experimental conditions, to molar absorptivity of protonated copper $[Cu(HL)]^-$ complex. The complex species $[Cu(H_2L)]$ shows absorption maxima at wavelengths 596 nm ($\varepsilon = 296$ mol^{-1} L^{-1} cm^{-1}), 313 nm ($\varepsilon = 8100$ mol^{-1} L^{-1} cm^{-1}) and 275 nm ($\varepsilon = 7000$ mol^{-1} L^{-1} cm^{-1}) which do not change too much with solution acidity when various protonated complex species are present in the aqueous solution [19]. The detection limit of the determination was estimated to be equal to 2.2×10^{-6} mol L^{-1}. The calibration curve was also measured in presence of zinc(II) of concentration 0.01 mol L^{-1} (Figure 2b) and in presence of divalent transition metal ions of concentration 0.005 mol L^{-1} (Figure 2c). The slopes of the calibration curves are equal to (4380 ± 50) L mol^{-1} cm^{-1} (Figure 2b) and (4430 ± 60) L mol^{-1} cm^{-1} (Figure 2c), however, in the latter case, there is also an intercept (0.073 ± 0.005) due to the absorption of other metal complexes (mainly cobalt(II, III) and nickel(II)) [20, 21]. In this case, standard addition method is recommended for the analysis. The differentiation of absorbance to eliminate the signal of other metal ions contributing to measured absorbance is also applied [22]. Differentiating absorbance at 350 nm gives the following slopes of calibration curves (in L mol^{-1} cm^{-1}): -69.2 ± 0.8 (only Cu^{2+}), -70.9 ± 2.8 (Cu^{2+}, Zn^{2+}) and -69.7 ± 1.0 (mixture of metal ions Zn^{2+}, Cd^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}). The values of calibration curve slopes are in an agreement, but a decrease of sensitivity of spectrophotometric determination can be observed. This leads to worse detection limit as a consequence of noise increase by differentiation procedure [22].

To verify a possibility of the copper(II) determination, analyses of artificial samples (aqueous mixture of metal ions) were performed. The results given in Table 1 are in accordance. In addition, analyses of spiked mineral water samples were done. The values 1.04×10^{-4} mol L^{-1} ("*Magnesia*") and 1.91×10^{-4} mol L^{-1} ("*Poděbradka*") obtained are in a good agreement. The samples of copper alloys were also analysed (Table 2) and a good agreement with the declared values was achieved.

Titration

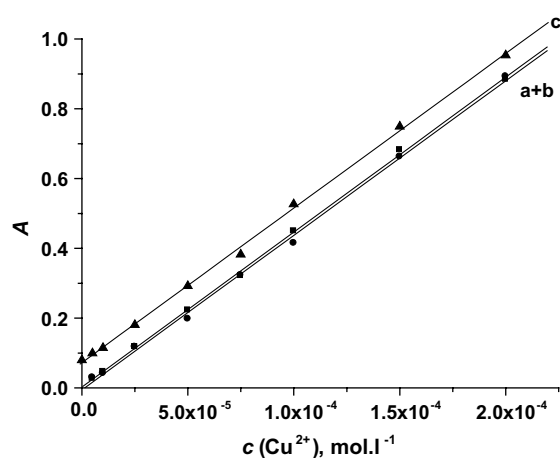To overcome the difficulties of spectrophotometric determination as a relative method, volumetric determi-

Figure 2. The calibration plots of spectrophotometric determination of copper in presence of various interfering ions ($\lambda = 310$ nm, $-\log [H^+] = 5.5$, $c_{dipon} = 4.587 \times 10^{-3}$ mol L^{-1}): (a) no interferent, (b) $c = 0.01$ mol L^{-1} Zn(II), (c) $c = 0.005$ mol L^{-1} Zn(II), Cd(II), Pb(II), Ca(II), Mg(II), Mn(II), Co(II), Ni(II).

Table 1. The results of spectrophotometric analysis of artificial samples

Sample	1	2	3
Cu (taken) $\times 10^5$ mol L^{-1}	10.00	2.00	6.00
Cu (found) $\times 10^5$ mol L^{-1}	9.80	1.97	6.09

The concentrations of elements presented in samples: Sample 1: $c(Zn^{2+}) = c(Cd^{2+}) = c(Pb^{2+}) = c(Mg^{2+}) = 0.02$ mol L^{-1}. Sample 2: $c(Zn^{2+}) = c(Cd^{2+}) = c(Ca^{2+}) = c(Mg^{2+}) = 0.02$ mol L^{-1}. Sample 3: $c(Zn^{2+}) = c(Cd^{2+}) = c(Pb^{2+}) = c(Ni^{2+}) = 0.01$ mol L^{-1}.

Table 2. The results of analysis of copper alloys

Alloy	1	2	3	4
Cu% (taken)	58.7	64.6	45.6	89.7
Cu% (found)[a]	60.0	65.3	–	–
Cu% (found)[b]	58.6 ± 0.9	$65._2 \pm 2.0$	45.6 ± 0.9	89.6 ± 0.6

[a] Spectrophotometric analysis (2 values).
[b] Volumetric analysis (3 values).
The percent content of interfering metals: Alloy 1(*Yellow brass*): Zn 34.67, Pb 0.89, Fe 0.19. Alloy 2(*Yellow brass*): Zn 31.11, Pb 1.97, Ni 0.37, Fe 0.50. Alloy 3(*Alpaca*): Zn 33.05, Ni 18.12, Pb 1.17, Fe 1.00, Sn 0.86. Alloy 4(*Phosporus copper*): P 9.77, Sn 0.76, Zn 0.26, Pb 0.40, Al 0.13, Fe 0.06.

Figure 3. An example of volumetric analysis of Alpaca alloy ($-\log$ $[H^+] = 5.5$, $V_{initial} = 10$ ml, $c_{dipon} = 4.587 \times 10^{-3}$ mol L^{-1}). The estimated equivalence volume is 0.396 ml.

nation of copper(II) by titration with *dipon* ligand was examined. In order to utilize the high molar absorptivity of copper(II) complex, a sensitive detection of equivalence titration point at maximum of absorption band by UV/VIS spectrophotometry was proposed. The logarithmic value of conditional constant should be higher than 8 (log $\beta_{cond} \geq 8$) to get sharp end-point of titration detected by UV/VIS spectrophotometry [23]. In addition, it was pointed out, that the ligands forming the complexes of reasonable stability (log $\beta_{cond} \geq 8$–12) are suitable for volumetric determination of metal ions while the systematic error is decreased to 0.1–0.01% [15]. This condition is fulfilled at $-\log [H^+] > 5$ (Figure 1). The value $-\log [H^+] = 5.5$ was chosen as optimal for selective copper(II) volumetric titration in order to shorten the reaction time in comparison to other divalent metal ions as it was discussed in the previous section. The wavelength 310 nm was chosen for the detection of titration end-point. The most of metal *dipon* complexes do not absorb at this wavelength and, therefore, they are not able to interfere the determination. When they absorb, the absorbance of the solution is only slightly increased (Figure 2c) and the differentiation of absorbance signal can be applied as it was demonstrated in the previous section. The high molar absorptivity of copper(II) complex formed ensures that the titration can be carried out at a low concentration level above the limit of detection determined in the previous section (i.e. 2.2×10^{-6} mol L^{-1}). An example of a volumetric copper(II) determination in Alpaca alloy is given in Figure 3. The copper(II) concentration determined in the sample is equal to 1.82×10^{-4} mol L^{-1}. This shows that analyte can be estimated on concentration level of tens and hundreds of micromol copper(II) per liter.

The proposed volumetric determination of copper(II) as a absolute method was verified on analyses of real samples. Spiked mineral water was used as a sample. Estimated copper(II) concentration in "*Magnesia*" sample is $(1.00 \pm 0.02) \times 10^{-4}$ mol L^{-1}. Comparison with given concentration (1.00×10^{-4} mol L^{-1}) shows a good agreement considering high concentration of some interfering ions (mainly magnesium(II) and carbonate species) in the solution.
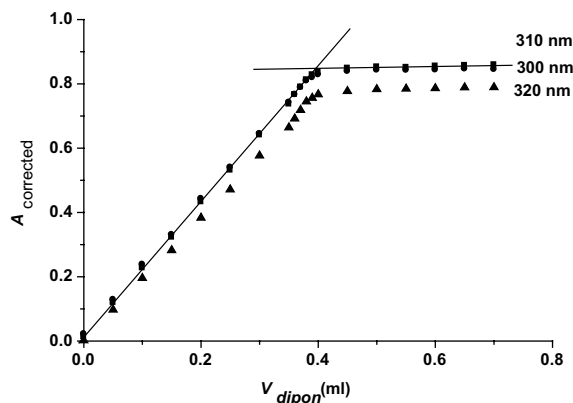
The copper alloys concerning zinc, nickel and lead as main interfering ions were analysed and the results are presented in Table 2. As can be seen from the results, a good agreement was achieved between the values of copper content declared and determined. This hypothesis of agreement between results was tested by *t*-test and the agreement was confirmed, i.e., there is no systematic error in the analysis by the proposed method. The results are interesting for analysis of copper-zinc alloys. No masking agents or indicators for the visualization of end-point detection are necessary in the proposed method, however, thiourea is usually employed as a masking agent for copper(II) in analysis yellow brass alloys [1].

Conclusions

The macrocyclic ligand *dipon*, as a new selective complexing agent, was tested for analytical applications of copper(II) determination. Spectrophotometric determination was optimized and optimal experimental conditions ($-\log [H^+] = 5.5$, $c_L \approx 5 \times 10^{-4}$ mol L^{-1}) were found. The analysis is valid in dynamic concentration range $(5$–200$) \times 10^{-6}$ mol L^{-1} with detection limit 2.2×10^{-6} mol L^{-1}, i.e. 0.13 μg mL^{-1}. The proposed method is simple, fast and it is not sensitive to the presence of other metal ions. Therefore it can be used for monitoring of quality of tap water (copper(II) concentration should be lower than 1.00 μg mL^{-1}). Volumetric determination of copper(II) with standardized *dipon* solution can be used for copper(II) determination at micromolar concentration level without any necessity to sequester the interfering metal ions as it is usually required in chelatometric volumetric determination with *edta*. The sharp end-point of titration can be followed by UV/VIS spectrophotometry at absorption maximum due to high molar absorptivity of copper(II) complex formed (4380 ± 50 L mol^{-1} cm^{-1}). Both methods were tested

on artificial and real samples (spiked mineral waters, alloys) and gave satisfactory results without any systematic error.

Acknowledgements

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