

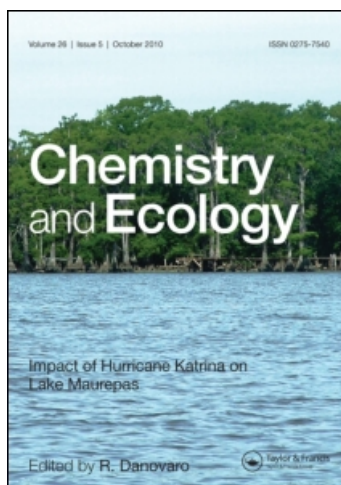
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## Chemistry and Ecology

Publication details, including instructions for authors and subscription information:

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**To cite this Article** Legittimo, Paola Cellini and Pantani, Francesco(1986) 'Complexing Capacity of Thermal Waters of Montecatini Terme (Italy)', *Chemistry and Ecology*, 2: 2, 95 – 102

**To link to this Article:** DOI: 10.1080/02757548608070826

**URL:** <http://dx.doi.org/10.1080/02757548608070826>

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# Complexing Capacity of Thermal Waters of Montecatini Terme (Italy)

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(Received July 30, 1984; in final form October 25, 1984)

Two typical waters from thermal springs of Montecatini Terme—used as therapeutical beverages—exhibit a small complexing capacity towards  $\text{Cu}^{2+}$ . By differential pulse anodic stripping voltammetry the following values were found:  $0.46 \mu\text{mol l}^{-1}$  and  $0.10 \mu\text{mol l}^{-1}$ , respectively for *Regina* and *Rinfresco* waters.

Owing to the presence of a small amount of complexed copper in the original samples, the complexing capacity has to be regarded as residual capacity. In bottled waters from the same springs no complexing capacity was detected. Values of formation constants for copper complexes are given. No residual complexing capacity for  $\text{Cu}^{2+}$  was displayed for *Tamerici* and *Tettuccio* thermal waters.

## INTRODUCTION

The waters of Montecatini Terme have always been a source of interest for doctors and hydrologists because of their therapeutic properties as laxative beverages, well known all over the world. Although their origin remains partly unclear (Coradossi and Martini, 1965), the chemical composition of the salts dissolved in them is known (Martini and Cellini, 1977). The high concentration of the main components (sodium chloride, calcium and magnesium sulphate) has been generally pointed out, but the importance of minor components has not been equally stressed. Particularly, the possible presence of organic substances capable of

complexing metallic ions has never been considered. And yet, the knowledge of the complexing capacity must be seen nowadays as an essential parameter for the formulation of correct biogeochemical models (Siegel, 1971; Stumm and Bilinski, 1972; Sunda and Hanson, 1979), as well as to establish the toxicity of the metals which are present in natural waters (Davies *et al.*, 1976; Andrews *et al.*, 1977; Gächter *et al.*, 1978).

The data existing in literature (Hart, 1981) refer above all to lake and river waters, where environmental pollution often markedly increases the concentration of organic material. Much less is published on the qualities of potable and curative waters. The authors of the present paper have tested the most typical thermal waters of Montecatini Terme, with the aim of checking if and in what amount these waters show a complexing capacity deriving from organic material.

Invariably natural systems are highly complex solutions, and analytical techniques, although becoming increasingly accurate and selective, cannot avoid a preliminary manipulation of the sample, often resulting in the sometimes irreversible alteration of the initial condition. The differential pulse anodic stripping voltammetry (DPASV) technique which was used in the present work, is outstandingly suited for this kind of analysis.

## APPARATUS AND REAGENTS

The voltammetric measurements were carried out with an AMEL Model 471 Multipolarograph. The electrochemical cell contained a hanging mercury drop working electrode (Microdoser E 410 Metrohm), a platinum wire counter-electrode and a saturated mercurous sulphate reference electrode. The working characteristics for the voltammetric measurements were as previously (Cellini *et al.*, 1980): electrolysis time 4 min at a potential of  $-1.00$  V/SSE with stirring at 500 rpm; pulse amplitude  $\Delta E = 50$  mV; scan rate  $10$  mV s $^{-1}$ ; quiescent time 30 s.

"Suprapur" reagents (Merck) were generally used or Analytical Grade reagents purified by electrolysis on a mercury cathode. Solutions were prepared by using water redistilled in quartz apparatus. Cu $^{2+}$  solutions at concentrations lower than  $1 \times 10^{-4}$  M were prepared daily. In the intervals between series of measurements, solutions of  $\sim 1$  M HNO $_3$  or HClO $_4$  were maintained in the voltammetric cell to remove any residual metal traces from cell walls and/or electrode surfaces.

## ANALYTICAL PROCEDURE

The measurement of the complexing capacity of a water (Chau *et al.*, 1974) is based on the amount of cupric ion which can be bound by organic ligands through direct complexation and/or substitution reactions. The complexation of the ligand with  $\text{Cu}^{2+}$  is complete in practical terms if the competing reactions due to the presence of other metals are negligible. Copper was chosen as the indicator cation to react with the miscellaneous ligands found in natural water because of its strong and non-specific association capability. The amount of  $\text{Cu}^{2+}$  "taken up" by the sample will be an indicator of the concentration of active ligands ( $C_L$ ) available for complexation.

$C_L$  is understood (Freeman, 1973) as the resultant of individual functional groups which act independently as ligands, and, because of the complexity of these molecules, the functional groups can represent a great variety of forms and molecular weights.

The practical measurement is carried out by adding to the sample small quantities of a solution with a known concentration of  $\text{Cu}^{2+}$ ; non-complexed  $\text{Cu}^{2+}$  is then determined with the DPASV technique. The instrumental response, in the presence of complexing capacity, is low or even non-existent if the complexes are electrochemically inactive. After the binding sites of the sample have been saturated with  $\text{Cu}^{2+}$ , the peak current increases linearly along with further additions of the metal; the intercept of the two linear trends marks a  $\text{Cu}^{2+}$  concentration which, with a conventional ratio metal:ligand = 1:1, corresponds to the above mentioned  $C_L$  concentration.

The waters examined (named *Regina*, *Rinfresco*, *Tamerici* and *Tettuccio*) were collected directly from the springs and stored at a temperature of  $\sim 4^\circ\text{C}$  in polyethylene containers. The measurements were carried out within 24–48 hours, although samples kept in storage for over three months did not show any alterations of their complexing capacity. The additions of  $\text{Cu}^{2+}$  were made after a 1 M acetic acid–2 M acetate buffer had been added to the sample. It was noted that the normal deaeration time of about 15 min was enough to reach a constant peak current. The rapidly attained equilibrium between  $\text{Cu}^{2+}$  and complexing agents made it possible to make additions directly in the cell, without having to allow for stabilization periods as in the procedure for lake waters by Chau *et al.* (1974).

## RESULTS AND DISCUSSION

The most representative results for complexing capacity were obtained with *Regina* water. The typical response illustrated by plotting the voltammetric peak current *vs.* the various additions of  $\text{Cu}^{2+}$  is shown in Fig. 1. Two straight lines of different slope are detectable: the segment A–B corresponds to the range in which the metal cation is complexed, although labily, by the ligands in the sample; subsequently the line B–C represents the additions of  $\text{Cu}^{2+}$  exceeding the complexing capacity. The intercept of the two lines, obtained as the average of four determinations, corresponds to an analytical copper concentration ( $C_M$ ) of  $0.46 \mu\text{mol l}^{-1}$ , and therefore, due to the assumed metal:ligand stoichiometry of 1:1, this is the value of the complexing capacity of the *Regina* water.

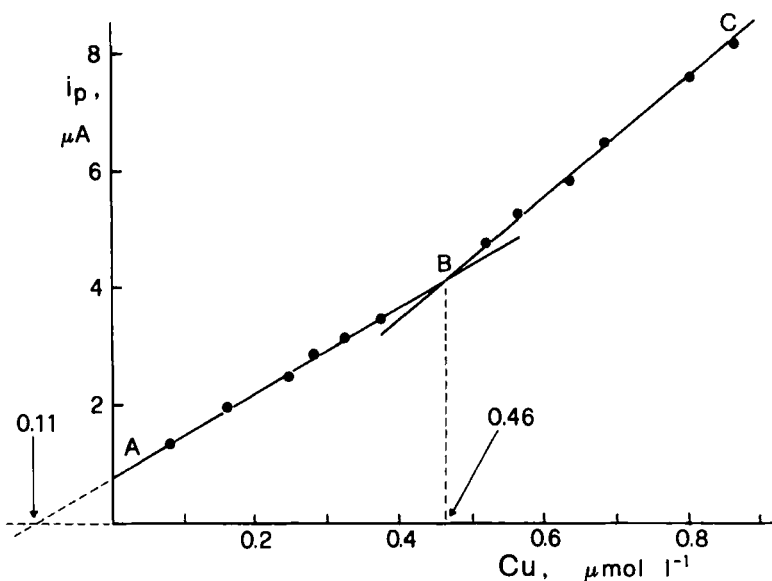


FIGURE 1 Variation of peak current by adding  $\text{Cu}^{2+}$  to *Regina* water.

Figure 1 shows that the peak current  $i_p$  is not equal to zero on the starting point of the titration; this indicates that the sample originally contains copper already involved in complexation equilibria, so that

the  $C_L$  value of  $0.46 \mu\text{mol l}^{-1}$  identifies more exactly the *residual* complexing capacity. The determination of copper already present in the water was carried out as previously by slow wet oxidation with  $\text{HNO}_3 + \text{HClO}_4$  (Piccardi and Cellini, 1974). The residue after mineralization was dissolved in acetate buffer and examined by voltammetry: the average of four determinations gave a value for the metal concentration  $C_M$  of  $0.14 \mu\text{mol l}^{-1}$ . On the other hand, the intercept of the line A-B with the X-axis in Fig. 1 gives the value  $C_M = 0.11 \mu\text{mol l}^{-1}$ . The slight difference between the two values, beyond the usually unavoidable errors of every method for the determination of trace metals, could indicate the possible presence (around  $0.03 \mu\text{mol l}^{-1}$ ) of chemically inactive copper complexes. According for the calculation of the formation constant  $K_{ML}$  of the complex between  $\text{Cu}^{2+}$  and ligand, the *total* concentration of the latter  $C'_L$ , which must be considered, does not correspond to the intercept B of the two lines in Fig. 1, but rather to the addition of the already calculated  $C_L$  and the one corresponding to the analytical concentration of the copper contained in the sample:

$$C'_L = 0.46 + 0.11 = 0.57 \mu\text{mol l}^{-1}.$$

A similar correction must be made for  $C_M$ . The calculation procedure applied was described by Shuman and Woodward (1977), whose work should be consulted for further details. The value of  $K_{ML}$  from the average of four determinations on the *Regina* water is  $7.6 \times 10^5 \text{ l mol}^{-1}$ . Despite this relatively high  $K_{ML}$  value, owing to the very weak concentration of the ligands the product  $K_{ML} \times C'_L$  is only 0.43; still according to Shuman and Woodward's mathematical approach, this value seems to be near the minimum detectable limit for the method.

Similar tests conducted on the *Regina* water after filtration through a microporous membrane of pore size  $0.45 \mu\text{m}$ , gave practically the same results, thus showing that the complexing capacity was not due to particulate matter. On the contrary, tests conducted on the same water bottled in the glass containers used for sale did not show the presence of any complexing capacity, since no intercept in the plot of  $i_p$  vs.  $C_M$  was detected.

The analysis showed relatively high concentrations of  $\text{Cu}^{2+}$  already present in the samples, up to  $0.62 \mu\text{mol l}^{-1}$  for a water bottled one year before. This constitutes at least a qualitative evidence that, either during the bottling or through exchange reactions with the glass of the bottle, an enrichment of the metal content takes place. Therefore, the

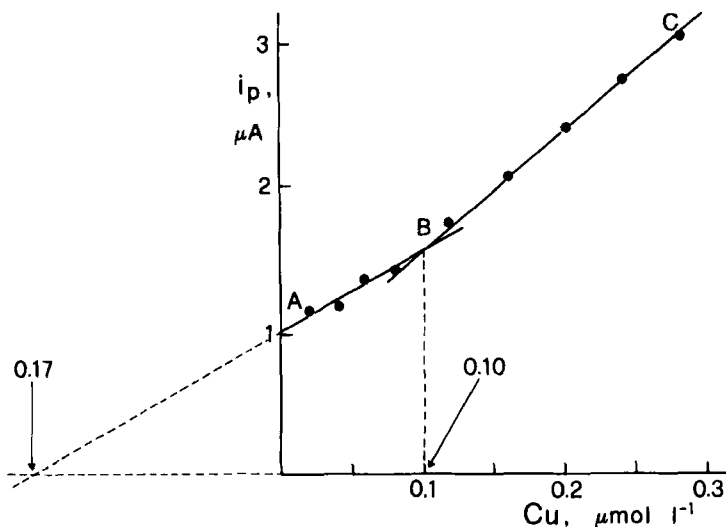


FIGURE 2 Variation of peak current by adding  $\text{Cu}^{2+}$  to *Rinfresco* water.

ligand sites for bottled water would be already saturated by the metal contained here in a much higher quantity than in the water taken directly from the spring. This phenomenon can be considered nothing more than an indication, since only a very prolonged survey based on many samples could provide the data for a deeper statistical evaluation.

As for the *Rinfresco* water, the resulting diagram shows also in this case two straight lines if  $i_p$  is plotted vs.  $C_M$  (Fig. 2, where an enlarged scale is employed). The residual complexing capacity is rather low:  $C_L = 0.10 \mu\text{mol l}^{-1}$ . The water already contains a  $C_M$  equal to  $0.17 \mu\text{mol l}^{-1}$ , confirmed by the mineralization of the sample; therefore the total complexing capacity is  $C'_L = 0.27 \mu\text{mol l}^{-1}$ . With the above mentioned procedure the formation constant was calculated as  $K_{ML} = 1.4 \times 10^6 \text{ l mol}^{-1}$ , being the average value of four determinations.

The samples of *Tamerici* and *Tettuccio* waters did not display any residual complexing capacity. In particular the *Tettuccio* water showed a copper content of  $0.20 \mu\text{mol l}^{-1}$ ; evidently, this concentration can satisfy the whole complexing capacity possibly existing in the sample.

Another point must be stressed: in the determination of the complexing capacity of a water, it would be desirable, if possible, to conduct the tests at the original pH of the sample. However Montecatini Terme

waters have a high content (4.9 to 11.0 m.equiv.  $l^{-1}$ ) of bicarbonate ion, while pH is 6.4 to 7.1; therefore, since deaeration by a current of  $N_2$ —necessary for voltammetric measurements—promotes the removal of  $CO_2$ , there is a risk of precipitation of carbonate salts. Shuman and Woodward (1974) tried to carry out deaeration by a  $N_2$  current enriched with  $CO_2$  to keep constant the initial pH but the results were not completely satisfactory. Therefore in the present authors' opinion, the method proposed by Chau and Lum-Shue-Chan (1974) using an acetate buffer (pH 4.7) appears to be the most reliable for this application. Inevitably, in such a medium, the values of the formation constants which are calculated must be considered *conditional*: however the acetate complexes of copper are so labile that they practically do not compete with the complexing capacity of the water.

Finally Pb(II) and Fe(III) have been shown experimentally (Chau *et al.*, 1974) to interfere with the determination of the complexing capacity, if present in minimum concentrations of 10 and 25  $\mu\text{mol } l^{-1}$ , since they form more stable complexes which copper cannot displace or can displace very slowly. This situation, frequent in lake waters, does not apply to the thermal waters examined in this paper.

## CONCLUSIONS

This preliminary survey shows clearly that the determination of the complexing capacity, both residual and total, can be a useful parameter for the characterization of thermal waters used as medicinal beverages. Among the pharmacological characteristics of the waters examined, the amount of residual complexing capacity is an important safeguard against any toxic effects produced by the presence of heavy metals as aquo-ions and to some extent a protection against metals introduced in handling. Under certain circumstances however, the complexation of beneficial elements in medicinal or potable waters could be regarded as a disbenefit.

Among the thermal waters of Montecatini Terme, *Regina* and *Rinfresco* waters showed some residual complexing capacity for  $Cu^{2+}$  but no excess complexing capacity was demonstrable for *Tamerici* and *Tettuccio* waters. Further analytical research into the possibility of conducting measurements at the pH values of the natural solutions is advocated as a necessary corollary.



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