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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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FINAL DESTINATION OF CADMIUM FOUND IN CONTAMINATED SEWAGE SLUDGE IN MAIZE-CULTIVATED RED NITOSOIL

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***ABSTRACT**. Remains of human activity, such as sewage sludge, caused by population growth, are a challenge to the environment and need urgent solutions. Cadmium from contaminated biosolid (sewage sludge) in Red Nitosoil, in PVC tubes (10 cm diameter and 80 cm height) located in greenhouse, has been analyzed. Natural biosolid in one treatment (control), cadmium-contaminated biosolid in two treatments (2,500 and 5,000 $\mu g\ g^{-1}$); cadmium- and lead-contaminated biosolid in other two treatments (2,500 Cd + 2,500 Pb and 5,000 Pb $\mu g\ g^{-1}$ respectively) were added to the 0 – 20 cm soil surface layer. Maize was the test plant in the triple replication experiment. The aerial part of maize plants, samples of surface soil (0 – 20 cm) and that within the tubes, divided into internal and external samples of each tube, were harvested seventy-five days after sowing. After the preparation and nitropercloric digestion of samples, Cd concentrations were measured by atomic absorption spectrometry. Cd concentrations in maize were within phytotoxic tolerance. There was no significant difference among treatments in the production of plant dry matter. Highest Cd concentration was found in the 0-20 cm soil layer and differed significantly from the rest.*

Key words: heavy metal; percolation; organic residues; pollution; cadmium.

***RESUMO**: Os resíduos da atividade antróprica em sociedade, como o lodo de esgoto, são desafios ambientais do crescimento demográfico que necessitam soluções. Com este objetivo foi estudado o destino do cádmio do lodo de esgoto (biossólido) contaminado em Nitossolo Vermelho, em casa de vegetação, em tubos de PVC (10 cm de diâmetro e 80 cm de altura). À camada superficial de 0 a 20 cm foi incorporado: o biossólido natural num tratamento (testemunha); biossólido contaminado com cádmio em dois tratamentos (2.500 e 5.000 $\mu g\ g^{-1}$); e contaminado com cádmio mais chumbo em outros dois tratamentos (2.500 Cd + 2.500 Pb e 5.000 Cd + 5.000 Pb $\mu g\ g^{-1}$, respectivamente). No experimento com três repetições foi usado o milho como planta teste. Após 75 dias da semeadura coletaram-se: a parte aérea das plantas de milho, as amostras de solo da superfície (0-20 cm) e dos tubos-sonda que foram divididas em amostra interna e amostra externa de cada tubo-sonda. Após a preparação e digestão nitro-perclórica das amostras, as leituras das concentrações de Cd foram feitas pelo método de espectrometria de absorção atômica. As concentrações de Cd nas plantas de milho apresentaram-se dentro dos limites fitotóxicos. Na produção de massa seca das plantas não houve diferença significativa entre os tratamentos. No solo, a maior concentração de Cd foi encontrada na camada de 0-20 cm, que, diferenciou-se significativamente das demais.*

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INTRODUCTION

Mankind learned by experience that soil produced less and less when continually cultivated. Consequently humans started to adopt certain agricultural practices, currently still in use, such as manuring, liming, crop rotation and others[1]. The addition of fertilizers to soil provides important nutrients to plants, namely, nitrogen (N), phosphorus (P) and potassium (K) which may be in default in the soil[2].

Population growth and the subsequent appearance of urban centers provided the dumping of human residues produced by development. Needless to say, this gives rise to environmental pollution that affects the general biota and man himself[3, 4]. Urban sewage[5], whose treatment causes sewage sludge[6], also known as biosolid, is of special importance. Through their penetration into the soil its components form a chain in the cycle and influence all forms of life. Pollutants, known as heavy metals[7], are among their components. Cadmium, the heavy metal currently under analysis, has been added to the environment in significant quantities with residues of mining, foundries, industrial refuse, sewage sludge and others[8]. On the other hand, studies are extant on the possibility of using sewage sludge in agriculture as organic manure even though it may have been contaminated by heavy metals [9, 10, 11].

Cd is naturally encountered in the soil as the product of rock meteorism whereby it is released. Under heavy oxidization cadmium oxidized mineral forms are CdO and $CdCO_3$[12] and its most important valence in the natural environment is 2+.

In soil solution Cd^{2+} is rapidly divided among the mineral, organic and solution phases. In fact, Cd^{2+}, and probably other metallic ions such as Zn^{2+}, is associated with water and forms a hydration complex. Ion Cd^{2+} is Lewis's strong acid and, associated with humidity, may cause the dissociation of protons. Cd may also exist in soil solution as a complex ion associated with other ligands. In soil solution the most important compounds are Cl^-, SO_4^{2-}, HCO_3^-, or organic links. Cd may also combine itself with ammonia ions in the form of $[Cd(NH_3)]^{2+}{}_{(aq)}$ or $[Cd(NH_3)_2]^{2+}{}_{(aq)}$ [13].

Brams and Anthony[14] analyzed cadmium absorption by wheat during a six-year period after addition of $CdCl_2$, concentration 7.5 kg ha^{-1}, to the soil. They noticed that concentration of cadmium greatly decreased in time. Data also indicated that 80% of Cd added was never recovered and failed to be detected up to 75 cm deep. The authors suggested that Cd was lost at the soil surface or at the soil sub-surface through the movement of soil particles.

Using doses 0, 20 and 40 t ha^{-1} of sludge complemented with 60, 80 and 100 kg ha^{-1} of N, P and K respectively, Silva (1995)[15] observed a linear increase in sugar cane production during the first year and did not detect any traces of heavy metals in the sugarcane broth.

Studies on the use of biosolids in soil for a variety of purposes [9, 10] are extant. There is, however, no agreement on the adequate dose for each culture, for each type of soil, for each type of climate, etc. This is perhaps due to difficulties in foreseeing the behavior of metals in different soil types and the nutrition requirements of each culture.

The current study analyzes the behavior of cadmium in contaminated sewage sludge applied to Red Nitosoil and its influence on maize culture.

MATERIALS AND METHODS

Soil

Red Nitosoil soil was collected in the region of the city of Maringá, PR, Brazil. Sampling occurred at depths 0 – 20, 20 – 40, 40 – 60 and 60 – 80 cm. Samples were placed separately in packages, taken to greenhouse and used in the experiment according to the exact positions in which they had been removed from the soil.

Table 1 shows chemical results of the soil's surface layer or arable section used (0 - 20 cm deep) prior to any treatment.

Table 1. Chemical characteristics of Red Nitosoil, 0-20 cm deep layer, used in experiment.

Soil	Cd(†)	Pb(†)	Fe(†)	Cu(†)	Mn(†)	Argila(‡)	silt(‡)	sand(‡)
	←		$\mu g\ g^{-1}$		→	←	%	→
RN(*)	4.50	39.2	119	25.9	448	52.0	27.0	21.0

(*) RN Red Nitosoil; (†) determination by atomic absorption spectrometry after nitric-perchloric digestion; (‡) Folk's granulometric classification[43] and calculation with method suggested by Suguio[44].

Table 2 shows characteristics of soil fertility of Red Nitosoil soil, layer 0 –20 cm depth, used in the experiment.

Table 2. Fertility of Red Nitosoil by chemical analysis (*).

Soil	pH		Al^{3+}	H^++Al^{3+}	Ca^{2+}	Mg^{2+}	K^+	P	C	CTC
	(H_2O)	($CaCl_2$)	←		$cmol_c\ dm^{-3}$		→	($\mu g\ g^{-1}$)	(%)	
TR	5.90	5.10	0.00	4.96	6.20	1.82	0.53	3.0	2.24	13.51

(*) Techniques: 1) pH in $CaCl_2$ 0,010 mol L^{-1} and pH in H_2O 1:2,5; 2) extractor Mehlich for K and P; 3) extractor KCl 1 mol L^{-1} for Ca^{2+}, Mg^{2+} and Al^{3+}; 4) [H^+ +Al^{3+}] method of SMP.

Sewage sludge, its properties and preparation

The Paraná Water Company (SANEPAR), Maringá sector, provided the sewage sludge which was collected at the Maringá Sewage Treatment Plant (ETE-2). The sludge was dried, ground and homogenized before analysis. After nitric-perchloric digestion of the samples, concentrations of K, Ca, Mg, Cu, Zn, Fe, Mn, Pb and Cd were obtained by atomic absorption spectrometry[16]. Whereas N concentration was evaluated by Kjeldahl method[17], P was determined by UV-Vis spectrophotometry of the phosphorus-molybdenum complex[18]. Determination of C occurred by oxidation of organic matter by $K_2Cr_2O_7$ in excess and in a concentrated sulfuric acid medium and posterior excess titration of potassium dichromate[19]. Table 3 shows mean values obtained from analyses in triple.

Humidity and liming (dry) of sewage sludge were undertaken immediately on reception, pH was corrected to approximately 6.0 by a mixture of calcium carbonate and magnesium carbonate in the proportion of 3:1. Quantity of lime added was determined by calibration curve[20].

Table 3. Chemical characteristics of original sewage slime (without chemical treatment) in experiment.

Material	N	P	K	Ca	Mg	S	C	Cu	Zn	Fe	Mn	Pb	Cd
	←				%		→		←		$\mu g\ g^{-1}$		→
Lodo(*)	2.92	0.82	0.18	3.08	1.02	0.32	24.3	146	1327	6128	262	122	3.50

(*) sewage sludge (biosolid).

Further, part of the sewage sludge was kept in its natural state, without any contamination, for control treatment; another part was contaminated by Cd (using $CdCl_2$) in $\mu g\ g^{-1}$, in 2,500 and 5,000 concentrations; still another part was contaminated by a mix of cadmium and lead, in $\mu g\ g^{-1}$, in 2,500 (Cd) + 2,500 (Pb) and 5,000 (Cd) + 5,000 (Pb) concentrations respectively. Lead was added as a possible interference factor in the behavior and final destination of cadmium in the system. Consequently sewage sludge was prepared for its incorporation to the arable soil layer (0 – 20 cm).

PVC (polyvinyl chloride) tube

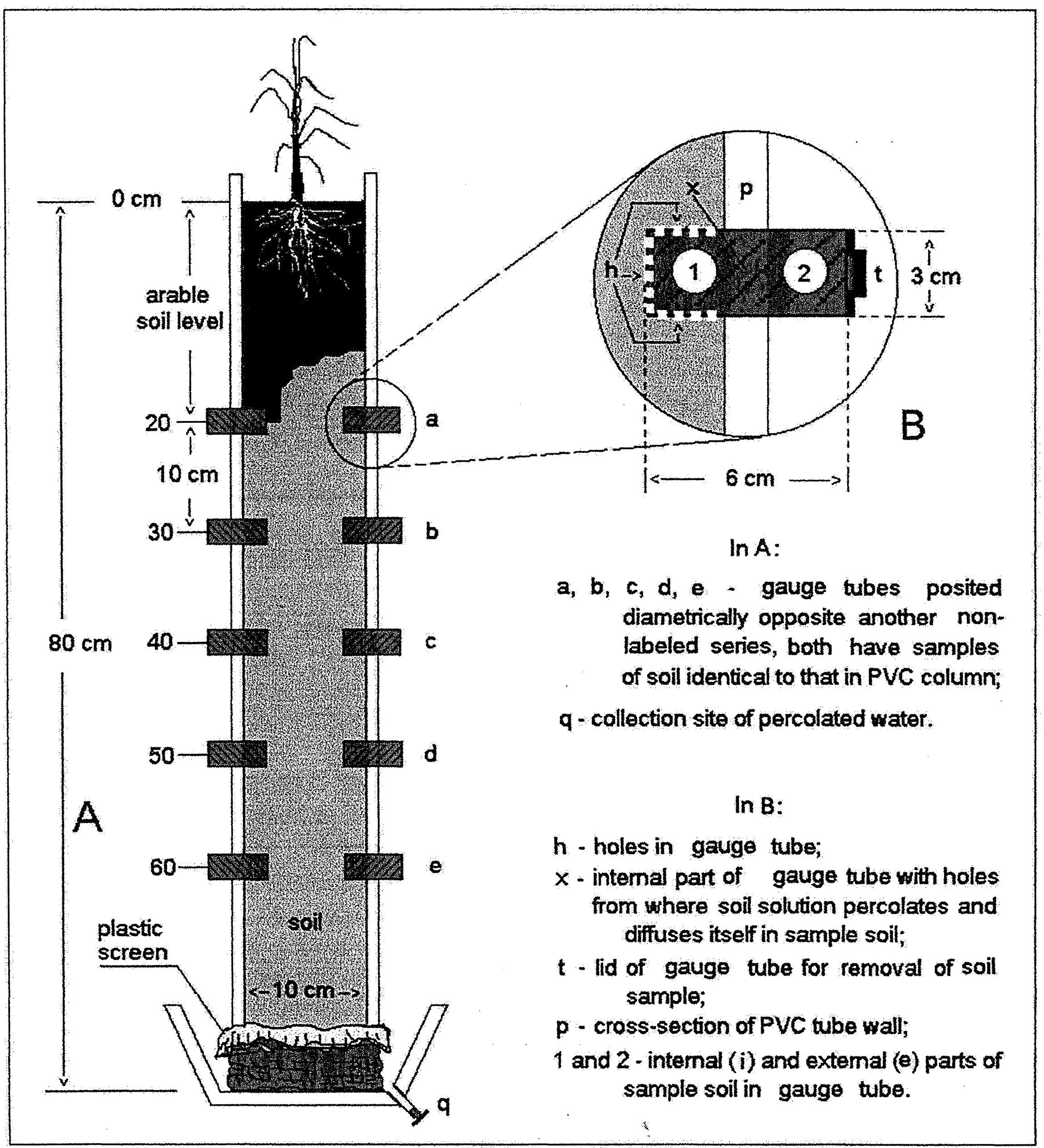
Figure 1 shows PVC tubes (10 cm diameter and 80 cm high) for used the experiment. Two series of gauge tubes were placed laterally, perpendicularly and diametrically opposite in the PVC tubes, at 10 cm depth, starting from 20 cm off the surface, as shown in Figure 1 – Part A. Gauge tubes collected soil samples at several depths without any damage to PVC tube or displacement of the soil column in the tube. Malleable plastic gauge tubes were fixed under pressure so that half remained in the interior of the PVC tube and the other half outside, with lid, as shown in Figure 1 – Part B. The inner side of the gauge tube was completely perforated with small holes so that soil solution could penetrate the gauge tube, or rather, percolate and diffuse itself throughout the soil and throughout that in the external part, as shown in Figure 1 – Part B. The existence of percolation and diffusion of the heavy metal cadmium could be verified at this sector.

Building, implantation and conduction of experiment

Three PVC tubes with gauge tubes were first prepared (Figure 1); they formed three replications for each type of sludge contamination. A total of 3 x (4 contaminations) + 3 x (1 control) = 15 PVC tubes was used.

A plastic screen was tied at the base and on the outside of each PVC tube to hold the soil in place and release the soil solution. Soil corresponding to the 60 – 80 cm layer was placed in each PVC tube together with the gauge tubes (e) filled with the same soil (Figure 1 – Part A). Identical process was used for the 40 – 60 layer soil with the respective gauge tubes (d, c) and for the 20 – 40 cm layer soil with the respective gauge tubes (b, a).

Sewage sludge contaminated with a 6 t ha^{-1} was added prior to placing the 0 – 20 layer soil in the PVC tubes, for each of the four types of contaminations above. This amounted to the following: 3 tubes with control (manured soil without pollutant); 3 tubes with contaminated soil containing Cd 2,500 $\mu g\ g^{-1}$; 3 tubes with contaminated soil containing mixture of Cd 2,500 $mg\ g^{-1}$ + Pb 2,500 $\mu g\ g^{-1}$; 3 tubes with contaminated soil containing a mixture of Cd 5,000 $\mu g\ g^{-1}$ + Pb 5,000 $\mu g\ g^{-1}$.



In A:

a, b, c, d, e - gauge tubes posited diametrically opposite another non-labeled series, both have samples of soil identical to that in PVC column;

q - collection site of percolated water.

In B:

h - holes in gauge tube;
x - internal part of gauge tube with holes from where soil solution percolates and diffuses itself in sample soil;
t - lid of gauge tube for removal of soil sample;
p - cross-section of PVC tube wall;
1 and 2 - internal (i) and external (e) parts of sample soil in gauge tube.

Figure 1. PVC tube (10 cm diameter; 80 cm high) with soil and test plant - maize: A – frontal vertical cut shows different soil layers and gauge tubes (**a**, **b**, **c**, **d**, **e**); B – amplification of frontal cut of gauge tube showing holes through which soil solution may percolate and diffuse itself through sampled soil in the internal (1) and external (2) parts.

After introducing non-contaminated (control) and contaminated sewage sludge in the first soil layer of each tube, the mixture was incubated for approximately 15 days, with humidity of each tube at 70% of field capacity and a 6.0 pH or whereabouts.

At the end of preparations for the experiment, 5 seeds of maize BR 300 were sown per vase. Pruning occurred with two plants per vase.

Tubes with maize plants were kept in a greenhouse. Plants were watered daily and position changes of tubes were done weekly at random. Watering occurred every seven days and double the amount of highest rainfall in the last 25 years in the region of Maringá (151.5mm) [21] was provided to percolate contaminant cadmium. Percolated solution was collected (Figure 1 – Part A), acidified at $pH<2$ with concentrated nitric acid and cadmium contents analyzed by atomic absorption spectrometry after pre-concentration by volume reduction in a water-bath.

Sample collection and analyses

Harvest of plants (aerial part) was done two and a half months after sowing, all at the same time; plants were washed and dried naturally and separately according to their distribution in vases. They were then placed in a buffer at 80°C for 48 hours[22]; weighted (Table 4) and ground in a Marconi MA 048 grinding machine. Plant samples (each formed by a set of plants) for analysis totaled 15.

A week after harvest soil samples from the 0 – 20 cm layer and from the gauge tubes were removed. The latter were divided into two parts, or rather, the internal part (i), corresponding to soil of the gauge tube placed within the PVC tube, and the external part (e) in which possible diffusion of the pollutant was analyzed. This totaled 150 soil samples of gauge tubes and 15 corresponding to the 0 – 20 cm layer.

Soil and plant samples, ground and dried at constant mass, were then decomposed by nitrate perchloride digestion.

Cadmium concentrations of the respective samples in duplicates were obtained by atomic absorption spectrometry, flame mode, according to handbook calibration rules and instructions by Welz & Sperling[23]. Atomic absorption spectrometer CG model AA 7000 ABC was used, with detection limit[23, 24] of 0.030 $\mu g\ mL^{-1}$. Tables 4 and 5 show the experimental results obtained.

Statistics

Experimental data was treated by variance analysis with Tukey test at 1% for mean comparison and SANEST was the software employed for statistical analysis.

RESULTS AND DISCUSSION

Rates 2,500 and 5,000 $\mu g\ g^{-1}$ of pollutant were randomly chosen due to the fact that they represent highly contaminated sludge that would be applied to soils and in 6 t ha^{-1} doses. If nothing occurs with the heavy metal in percolation and exportation by plants when applied to sludge in a certain soil, the biosolids may be applied to the soil without any further concern. Such an inference may be done, since cadmium, in the form in which it has been added, is available in soil solution without any previous mineralization of the sludge's organic matter.

Although lead is found naturally on the earth crust at mean values of 12.5 mg kg^{-1} [25] and 16 mg kg^{-1} [26, 27], it has been constant from the very beginning of human civilization[28]. In 1981 lead was the fifth element in world metal production ranking, following Fe, Cu, Al and Zn[29]. At present it is ubiquitous in the environment [30-35]. Since it is also found in sewage sludge, it has been added so that possible interferences in Cd behavior could be studied.

Table 4. Production of dry matter from plant's aerial part and cadmium concentration.

Treatments	Production in g (*)	Cd concentration in μg g^{-1}(†)
Control	4.22 a (‡)	0.80 b (‡)
Cd (2,500)	3.79 a (‡)	7.10 a (‡)
Cd (5,000)	3.52 a (‡)	6.71 a(‡)
Cd (2,500) e Pb (2,500)	3.82 a (‡)	6.70 a(‡)
Cd (5.000) e Pb (5,000)	3.35 a (‡)	9.20 a(‡)

(*) mean values of the experiment's three replications; (†) mean values of two analytic replications; (‡) means followed by different letters differ at 1% level of significance.

Table 5. Mean of Cd concentration (μg g^{-1}) in Red Nitosoil for triplicates of different treatments.

Depth (cm)		Treatments				
		Control	Cd (2,500)	Cd (5,000)	(Cd + Pb) 2,500(†)	(Cd + Pb) 5,000(‡)
Surface		4.94 a*	21.77 a*	31.88 a*	20.82 a*	32.31 a*
20	**i**	4.88 a*	4.86 b*	4.94 b*	4.89 b*	4.85 b*
	e	4.87 a	4.86 b	4.92 b	4.88 b	4.83 b
30	**i**	4.87 a	4.85 b	4.92 b	4.86 b	4.83 b
	e	4.86 a	4.85 b	4.89 b	4.86 b	4.82 b
40	**i**	4.86 a	4.85 b	4.88 b	4.83 b	4.80 b
	e	4.83 a	4.83 b	4.86 b	4.83 b	4.79 b
50	**i**	4.82 a	4.83 b	4.86 b	4.80 b	4.79 b
	e	4.80 a	4.82 b	4.86 b	4.77 b	4.77 b
60	**i**	4.73 a	4.80 b	4.83 b	4.76 b	4.77 b
	e	4.68 a	4.77 b	4.82 b	4.74 b	4.76 b

i – internal part of gauge tube; **e** – external part of gauge tube; (†) contamination of biosolid in treatment, in μg g^{-1}, for each element; (‡) contamination of biosolid in treatment, in μg g^{-1}, for each element; * means followed by different letters differ at 1% significant level.

Maize plants

Maize plants were harvested 75 days after germination since they exhibited certain deficiencies: leaves began to turn purple, probably due to P deficiency; later, they manifested yellowing symptoms (chlorosis), probably due to N deficiency, according to Kabata-Pendias & Pendias[36]. Table 4 shows the dry part of the aerial part of the plant. Variance analysis failed to show any significant difference in dry matter production.

Cd concentration in the aerial part of plant (Table 4) shows that Red Nitosoil soil had similar values, including treatments in which Pb has been employed as interference factor. It differed, however, from the control in which the least absorption by plant occurred owing to less availability or to low concentration.

Lake (1987)[37] states that absorption of Cd applied with sewage sludge immediately before planting is at least 10 times higher than that when sowing is done in sludge-treated soils during consecutive years.

According to Kabata-Pendias & Pendias (1992) [36], cadmium may have the following concentration rates in the dry tissues of mature leaves for different species: a) normal or sufficient concentration, from 0.05 to 0.2 $\mu g\ g^{-1}$; b) excessive or toxic, from 5 to 30 $\mu g\ g^{-1}$; c) tolerated in agronomic species, 2 $\mu g\ g^{-1}$. Experimentally obtained rates are found within the phytotoxic range (Table 4). Cadmium concentration in the control was lower than that tolerable, albeit above normal.

Cadmium in the soil

Results of Red Nitosoil soil treated with either contaminated or non-contaminated sewage sludge (Table 5) showed an accumulation of heavy metal at the surface (0 – 20 cm depth level) where contaminated sewage sludge was applied in all treatments. Heavy metals generally fix themselves at 0 – 20 cm depth layer, precisely the layer with the highest fertility index and, obviously, greatly used in agriculture[38].

Analyzing interactions between humus acids and heavy metals, Ladonin and Margolina (1997)[39] present a hypothesis for heavy metal retention. They admit a chemical fixation between the active sites of humus acids and metals.

Such a "fixation", or rather, a chemical link, occurs by the formation of external or internal layer complexes[40]. Interactions between cadmium cation and the simple or homologue composite ligand within the external layer are electrostatic according to [1]:

$$Cd_{aq}^{(2+)} + L_{aq} \rightleftarrows \{[Cd_{aq}^{(2+)} \underset{\substack{\downarrow \\ \text{electrostatic interaction}}}{\ldots} L_{aq}^{(n-)}]^{[(n-)+(2+)]}\}_{aq} \qquad [1]$$

where L is the ligand which may be either a simple composite (Cl $^{-}$, CO3^{2-}, PO4^{3-}, amino-acids etc) or a homologous composite (fulvic and humic acids, proteins, metallic oxides and hydroxides etc).

In the internal layer complexes the interaction between cadmium and the ligand is covalent [2]:

$$Cd_{aq}^{(2+)} + L_{aq}^{(n-)} \rightleftarrows \{[M \underset{\substack{\downarrow \\ \text{covalent interaction}}}{-} L]^{(n-)+(2+)]}\}_{aq} + x.H_2O \qquad [2]$$

In all treatments Cd concentrations comprising horizontal direction, external and internal parts of the gauge tubes, and vertical direction, 20 – 60 cm depth layer, did not have statistically significant differences. They were compatible with control and thus confirm that neither lixiviation nor diffusion of heavy metals occurred in these directions. A similar study with cadmium in Dark Red Latosol showed the same conclusion[41].

Although clay makes up 52% of soil (Table 1), its cationic change capacity amounts to 13.51smol$_c$ dm^3 (Table 2). This is rather low when compared to certain types of clay and shows slightly expansive clay[7].

Studies on metal movements in soils treated with organic residues suggest that less than 1% of metals may be lixiviated. These metals may either be adsorbed or made more complex, till changes occur in the system[42]. This fact has been detected in current experiment since cadmium was not found in percolation water in the soil of the PVC column when irrigation, imitating torrential rain, was executed weekly.

When data in Tables 4 and 5 are analyzed with regard to treatments for possible Pb interference in Cd, it has been observed that the former failed to change Cd behavior in any treatment.

CONCLUSIONS

The experimental results led to the following conclusions:

The heavy metal Cd in soil was retained at the arable soil level (0 – 20 cm depth) in all treatments.

No significant difference occurred in the production of dry matter from the aerial part of plants.

When Cd absorption by the aerial part of maize plants is taken into account, Cd concentration rate maintained itself at the starting level of phytotoxic concentrations.

Lixiviation and metal diffusion have not been observed in layers below the arable level.

Pb interference with Cd behavior has not been detected in any soil or plant parameter.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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A STUDY OF THE CORROSION INHIBITION OF CARBON STEEL IN AMMONIACAL MEDIA DILUTED BY N-CYCLOHEXYL BENZOTHIAZOLE SULPHEN AMIDE

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ABSTRACT

The inhibition effect of N-cyclohexyl benzothiazole sulphen amide (NCBSA) was studied on the corrosion of carbon steel in diluted ammoniacal solution at temperatures of 25 °C and 30°C.

The effects of the inhibitor on the corrosion were investigated and determined by using electrochemical measurements (curves of intensity - voltage). The efficiency of NCBSA increased with increase in concentration, but decreased with increase in temperature. Free energy of activation was determined from Arrhenius type equation. Experimental data fitted on adsorption isotherm of Langmuir type, while the results were correlated to the chemical structure of the inhibitor.

RESUMO

A inibição da corrosão do aço carbono por N-ciclohexil benzotiazol amida (NCBSA) em solução amoniacal diluída foi estudada á 25 e 30 °C. Os efeitos do inibidor foram estudados e determinados usando medidas eletroquímicas (curvas de intensidade-voltagem). A eficiência do inibidor (NCBSA) aumentou com a concentração e diminuiu com o aumento na temperatura. A energia de ativação foi determinada usando a equação de Arrhenius. Os resultados expereimentais seguem o isoterma de adsorção de Langmuir e foram relacionados com a estrutura do inibidor.

KEYWORDS: carbon steel, ammoniacal media, inhibitor, N-cyclohexyl benzothiazole sulphen amide

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INTRODUCTION

Before 1960, the treatment of the carbon steel corrosion in the systems of water cooling was based on inorganic inhibitors such as chromates, nitrates, polyphosphates and zinc salts.[1-3] The use of chromates is restricted because of their toxicity, while the nitrates are efficient in concentrations that economically disadvantageous, being also easily decomposed by bacteria.[3]

Particular attention has been given lately to the use of polyphosphates and their derivates.[4] The advantageous use of these compounds consists in the lack of toxicity. Moreover, only a concentration of a few ppm is necessary for the protection of great systems of water supply. Yet they can be media favourable for the development of microorganisms.

Ever since 1960 more advanced treatments based on organic compounds[5,6] have been proposed to improve protection against corrosion.

The efficiency of the corrosion inhibition by the organic compounds is closely related to the structure and the properties of the layer formed on the metal surface under experimental conditions. The process of the adsorption of the organic compounds is attributed to the effects of the functional groups grafted on aromatic nuclei.[7,8]

It appeared that the adsorption depended especially on the electronic structure of the molecule and that the inhibiting effect increased with the number of aromatic nuclei.

The organic compounds containing sulphur and nitrogen have been utilized for the corrosion inhibition of carbon steel in acid media, the results showing that the most inhibitors act through adsorption at the metal surface.[9-10] The power of adsorption and consequently the strength of the inhibiting effect are dependent on the nature of the organic compounds, on the nature of the metal and of corrosive medium.

The current investigation establish the role of NCBSA in improving the passive films resistance towards general corrosion of the carbon steel in diluted ammoniacal solution of 10^{-3} N concentration.

EXPERIMENTAL DETAILS

The sample chosen for investigation is carbon steel LC 35 having the following composition: C = 0.35%, Mn = 0.65%, Si = 0.25%, S = 0.035% and iron up to 100%. For all experiments the carbon steel samples were polished with sand paper, cleaned in water, degreased in ethilic alcohol and dried in warm air.

The corrosion medium was the ammoniacal solution of 10^{-3} N concentration in contact with air at a temperature of 25°C and 30°C.

The tested inhibitor was N-cyclohexyl benzthiazole sulphen amide (NCBSA) and the measurements were made for its concentrations of 10^{-4} M, 2×10^{-4} M, 3×10^{-4} M and 4×10^{-4} M.

The electrochemical measurements were made using a standard corrosion cell. The working electrode was a carbon steel plate with an area of 4 cm^2. A calomel-saturated electrode was used as a reference electrode and the auxiliary electrode was a platinum plate. Data were computerized.

RESULTS AND DISCUSSION

The polarization curves are presented in figure 1. As compared to the non-inhibited solution, the corrosion potential shifted towards positive values. The presence of NCBSA increases the anodic over-voltage and leads to a decrease in the corrosion current. Up to current densities of 5 mA dm^{-2} the anodic potentials present a slight increase towards higher positive values. At current densities higher than 5 mA dm^{-2} the increase in potentials is significant, which supposes the inhibitor desorption on electrode surface. The decrease in the corrosion current was associated with a significant shifting of the corrosion potential towards higher values. This suggests that when the inhibition is mixed type it is preponderently anodic. The Tafel segments in the curves of cathodic polarization have small slopes being in the vicinity of the cathodic current limit. The nature of this limit is probably determined by the total transfer of all the cathodic-reduced compounds such as: O_2, NH_4^+, H_3O^+. The retardation of the metal ionization by inhibitors is stronger than the stimulation of the cathodic process, the free corrosion potential of carbon steel significantly increasing with the increase in NCBSA concentration.

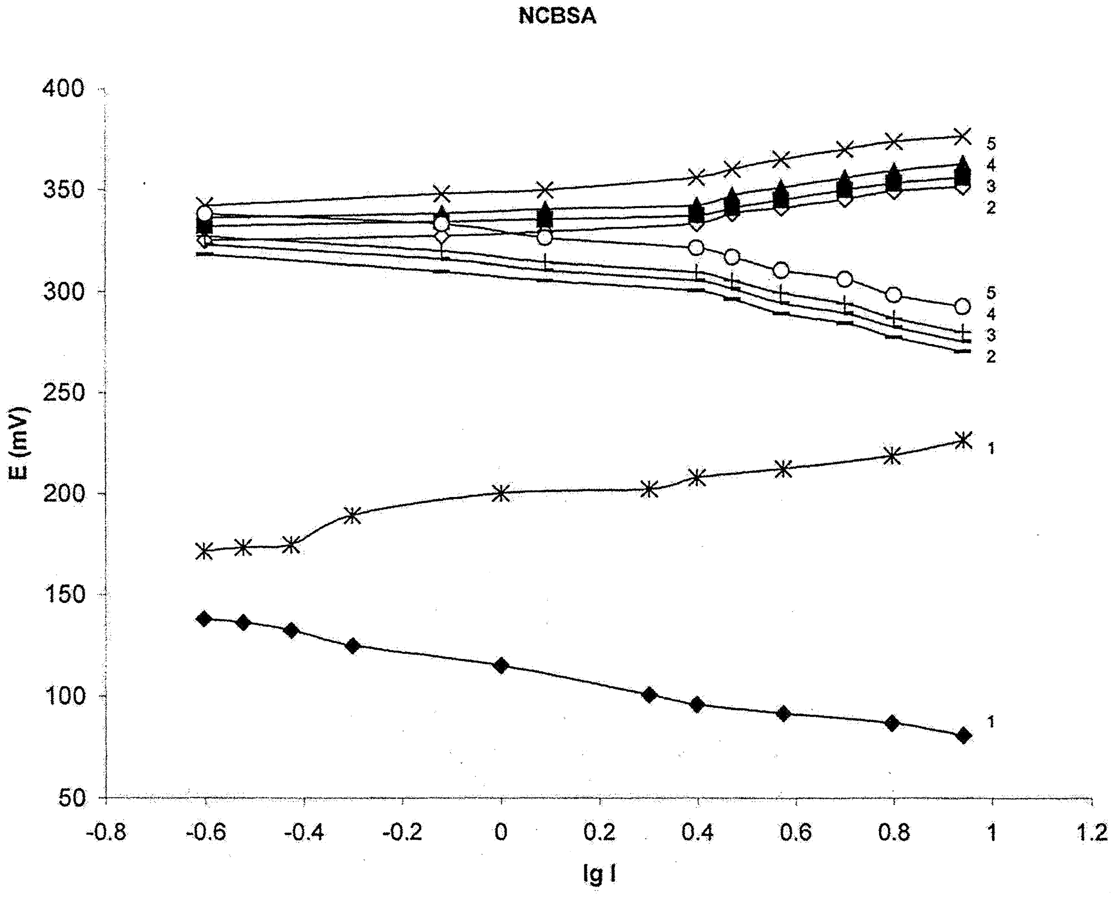

Figure 1. The polarization curves for carbon steel in ammoniacal solution 10^{-3} N in the presence of NCBSA at different concentrations: (1) 0.0; (2) 10^{-4} M; (3) 2×10^{-4} M; (4) 3×10^{-4} M; (5) 4×10^{-4} M.

In inhibitor solutions the steel remains active and behaves as an anode and dissolves after a Tafel-type slope b_a at 36±3 mV (figure 2)

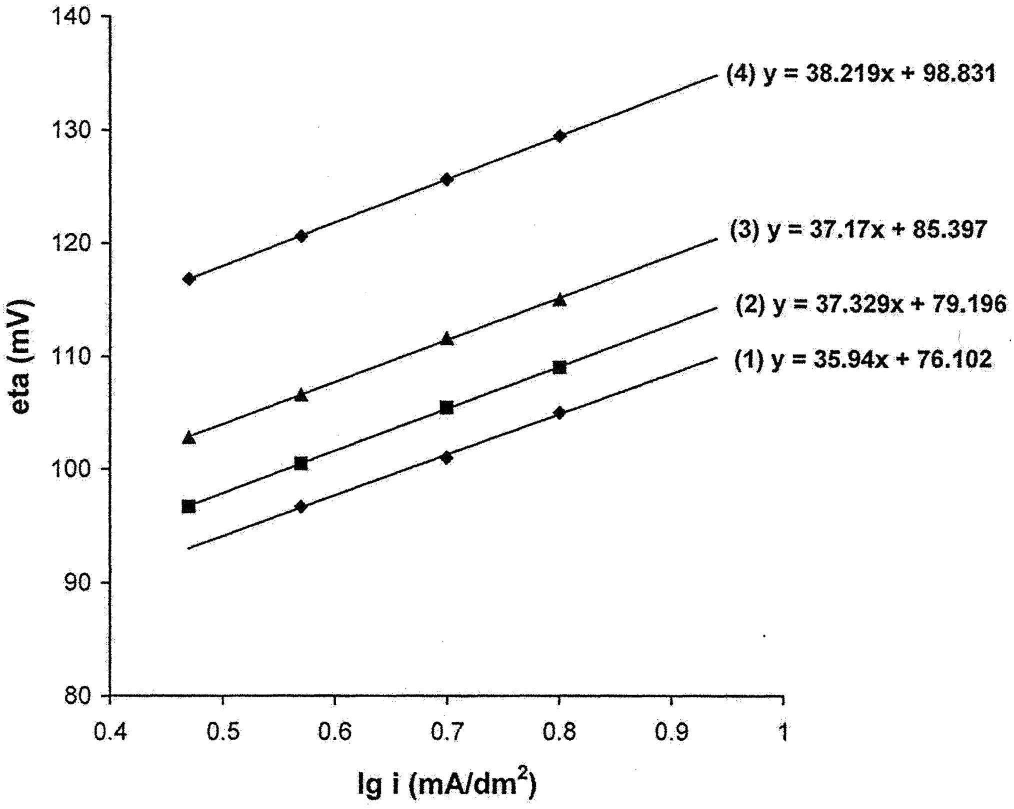

Figure 2. Graphical representation of $\eta = f(\lg I)$ for carbon steel in ammoniacal solution 10^{-3} M in the presence of NCBSA at different concentration: (1) 10^{-4} M; (2) 2×10^{-4} M; (3) 3×10^{-4} M; (4) 4×10^{-4} M.

The corrosion current can be calculated from Tafel-type equation with potentials far apart from the corrosion potential for a theoretical slope b_a equal to 2,3RT/zFα mV, as follows:

$\lg I_{cor} = 2.06 - 0.026(\eta_2 - \eta_1)$ (1), for the temperature of 25°C;
$\lg I_{cor} = 2.12 - 0.025(\eta_2 - \eta_1)$ (2), for temperature of 30°C,

where:

I_{cor} = corrosion current in the presence of inhibitor;
η_1 = galvanostatic over-voltage for non-inhibiting solution;
η_2 = galvanostatic over-voltage for inhibiting solution.

The efficiency of inhibition represented by the rate was calculated from the formula:

$$P = \frac{i_{cor_1} - i_{cor_2}}{i_{cor_1}} \qquad (3)$$

where: i_{cor1} = corrosion current for non-inhibiting solution

i_{cor2} = corrosion current for inhibiting solution
The results are presented in Table:

Table 1. The electrochemical parameters for carbon steel in ammoniacal solutions 10^{-3} N in the presence or absence of NCSBA, the percent P obtained from the galvanostatic polarization η and the corrosion rate at 25°C and 30°C.

	25°C					30°C				
C_{NCBSA}	0	10^{-4}	$2x10^{-4}$	$3x10^{-4}$	$4x10^{-4}$	0	10^{-4}	$2x10^{-4}$	$3x10^{-4}$	$4x10^{-4}$
E_{cor} (mV)	159	267	272	278	284	153	260	265	270	277
I_A (mA dm^{-2})	8.75	8.75	8.75	8.75	8.75	8.75	8.75	8.75	8.75	8.75
η (mV)	67	107	111.7	118.6	132	64	102.5	107.5	111.6	119
I_{cor} (μA dm^{-2})	116	10.5	7.9	5.3	2.3	132	14.5	10.8	8.5	5.9
P (%)	-	90.9	93.2	95.4	98	-	89	91.8	93.5	94.6
K_g (mg m^{-2} h^{-1})	8.1	0.74	0.56	0.37	0.16	9.3	1.02	0.76	0.6	0.42

The variation of the corrosion rate with an inhibitor concentration is presented in Figure 3. The corrosion rate decreases with the increase in the inhibitor concentration and increases with the increase in temperature, which indicates a stronger desorption of the inhibitor on the electrode surface. It is known from a previous work,[11] where the electrochemical measurements were associated with Mössbauer spectroscopy measurements, that in absence of the inhibitors the carbon steel surface is covered with a nonstoichiometric iron oxide layer.

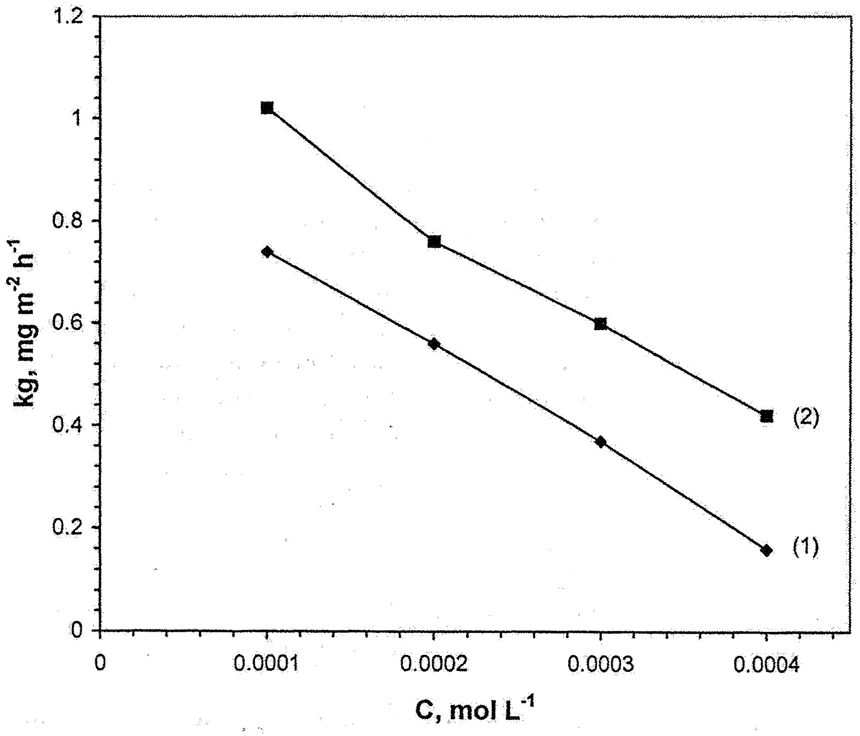

Figure 3. The variation of the corrosion rate with NCBSA concentration: (1) 25°C; (2) 30°C.

The investigation of the inhibition led to the conclusion that the experimental data fit an adsorption isotherm of Langmuir-type expressed by the relation:

$$\frac{\theta}{1-\theta} = Kc \qquad (4)$$

where: $\theta = P/100$
K = the equilibrium constant of the adsorption process;
c = the inhibitor concentration in the solution mass

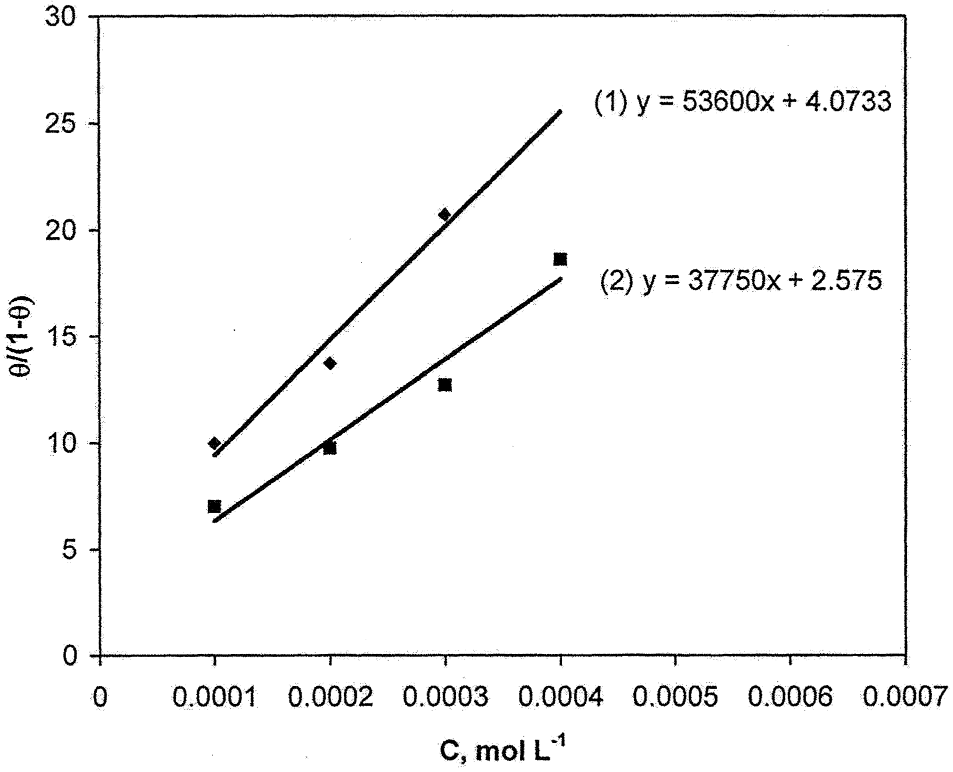

Figure 4. Langmuir-type diagram for corrosion inhibition of carbon steel in ammoniacal solution 10^{-3} N in presence of NCBSA at different temperatures: (1) 25°C; (2) 30°C.

Data are presented in Table 2. Figure 4 illustrates the results of a Langmuir-type diagram. The standard free energy of adsorption was calculated from the formula:

$$\Delta G_{ads}^{0} = -345.6 \cdot 10^{3} \lg \frac{K_1}{K_2} \qquad (5)$$

The values of K are relatively high indicating an electrostatic interaction between the double layer and the adsorbed molecules. The equilibrium constants of adsorption imply a more efficient adsorption at the temperature of 25°C than at 30°C. The values of ΔG_{ads}^{0} are negative, which shows the adsorption process takes place spontaneously. The activation energy characteristic to the corrosion inhibition was mathematically calculated from Arrhenius-type equation for tow different temperatures.

$$E_a = -345.6\cdot10^3 \lg\frac{k_{g_1}}{k_{g_2}} \qquad (6)$$

Table 2. The activation energy, the equilibrium constant and the standard free energy of adsorption for the carbon steel sample in ammoniacal solution 10^{-3} N in presence of NCBSA.

C_{NCSBA} (mol L^{-1})	E_a (kJ mol^{-1})	25°C		30°C		ΔG_{ads}^0 (kJ/mol)
		θ/(1-θ)	K (mol^{-1})	θ/(1-θ)	K (mol^{-1})	
0	21.5	-	53.6 x 10^3	0	3.7 x 10^3	-52.81
10^{-4}	48.6	9.98		7		
2 x 10^{-4}	45.8	13.7		9.75		
3 x 10^{-4}	72.5	20.7		12.7		
4 x 10^{-4}	144.8	49		18.6		

The values of the activation energy depend on the nature and concentration of the inhibitor.

CONCLUSIONS

Concurrently with the increase in the current density the anodic potentials of the steel electrodes in ammoniacal solution 10^{-3} N containing NCBSA are shifted towards higher values, while the cathodic potentials are shifted towards lower values. The presence of NCBSA in the corrosion medium increases the anodic and cathodic over-voltage and decreases the corrosion current. These changes increase with the increase in NCBSA concentration.

The decrease in the corrosion current was associated to a significant shift of the corrosion potential towards higher values. This suggests that when the inhibition is of mixed-type it is predominantly anodic.

NCBSA behaves as an inhibitor of generalized corrosion. The efficiency of inhibition increases with the increase in the NCBSA concentration, but decreases with the temperature increase.

Inhibition was associated with the NCBSA adsorption on the steel surface. Due to its great efficiency, it appeared that a complex was formed between NCBSA and different metallic cations in steel composition. These complexes can form passivating layers that are stable at the steel surface, thus decreasing the corrosion rate. The adsorption of these inhibitors on the steel surface fits the conditions of Langmuir-type isotherm of adsorption.

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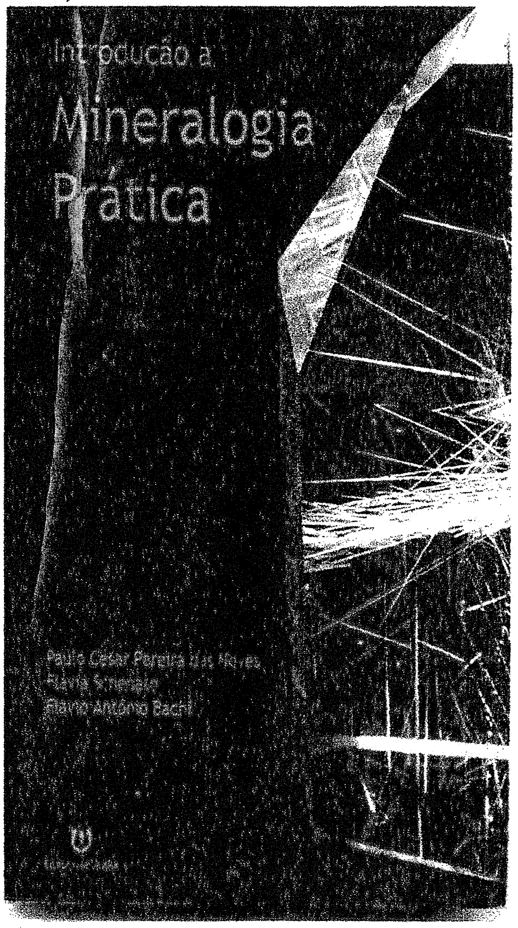
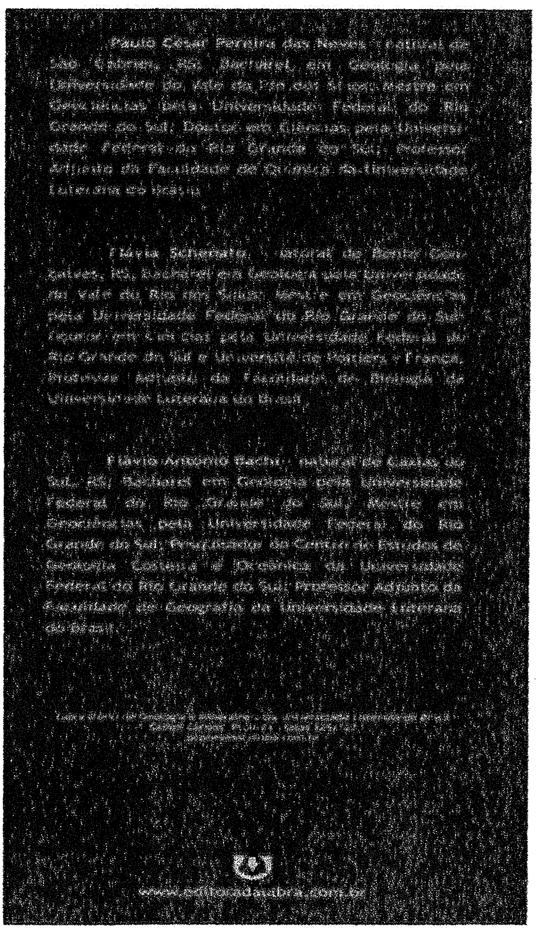
BOOKS/ LIVROS

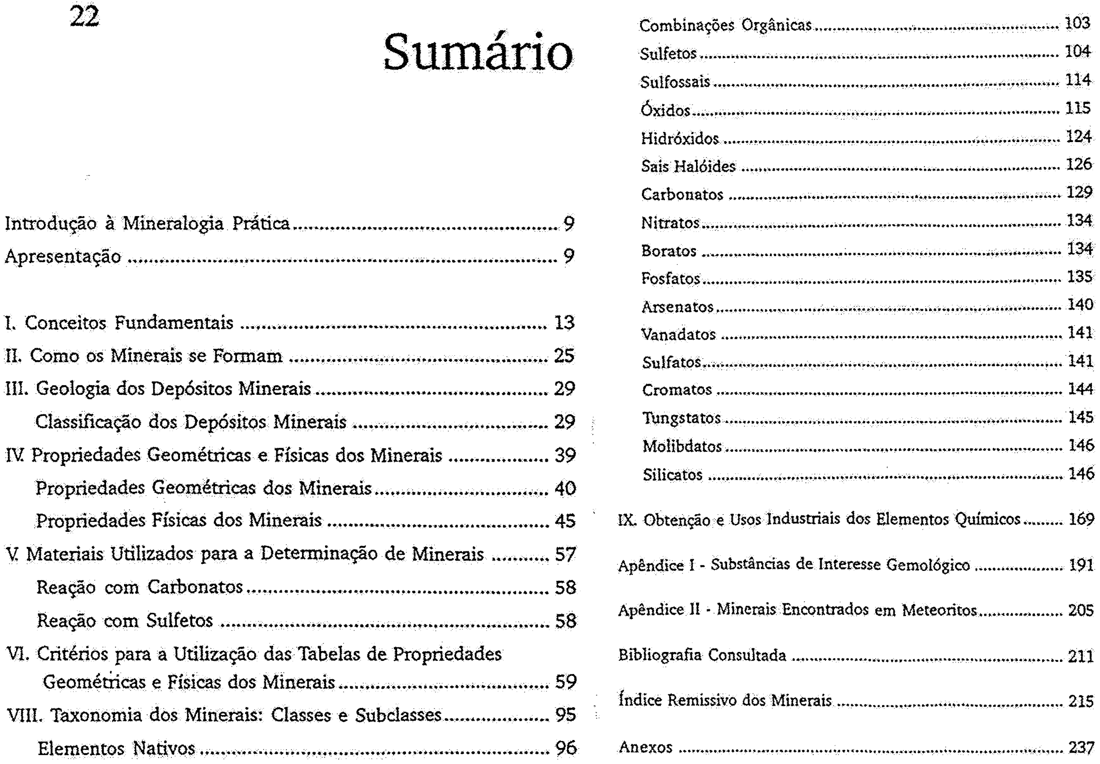
PAULO CÉSAR PERERIA DAS NEVES, FLÁVIA SCHENATO,
FLÁVIO ANTÔNIO BACHI, *"Introdução à Mineralogia Prática"*, Editora da
ULBRA, Canoas, RS, Brasil, 2003, 238p.

"Introdução à Mineralogia Prática" é um excelente livro que apresenta uma temática ampla e atualizada sobre os conceitos básicos de mineralogia. O manual apresenta a classificação sistemática dos minerais baseada nas normas mais recentes da Associação Internacional de Mineralogia (International Mineralogical Asssociation – IMA).





Como pode ser visto no Sumário, o manual tem caráter introdutório, trata de conceitos fundamentais e não aborda métodos e técnicas analíticas mais modernas utilizadas nos estudos dos minerais.



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O livro, acima de tudo é útil para todos os estudantes universitários das ciências, incluindo Química, Geografia, Física, Agronomia, Engenharia e Biologia, além da Geologia.

As ilustrações fotográficas são de minerais pertencentes à Coleção de Minerais do Museu de Ciências da Universidade Luterana do Brasil (CMULBRA) e amostras particulares do Prof. Dr. Paulo César Pereira das Neves (CMPN). Lamentavelmente, as dezessete (17) estampas coloridas foram amontoadas num anexo no fim do livro, ao invés de ser incluídas nos lugares apropriados no texto. Além disso, elas são cópias medíocres das fotografias originais e tiram quase toda a beleza e brilho dos minerais.

Certa vez, um Velho Índio, nosso amigo do Novo México – Terra do Encanto, dizia que tem quatro coisas que são verdadeiramente bonitas na Natureza, que fascinam e encantam com a sua beleza, brilho e magia. São as estrelas, as flores, os minerais e os olhos cintilantes de mulheres bonitas.

Aparentemente, a sabedoria de alguns não chegou em certos lugares mais longínquos e distantes do Planeta Terra e não alcançou outros, incluindo editores, mais preocupados com lucros e aspectos financeiros.

O livro é o resultado de anos de experiência dos três autores no ensino de mineralogia.

Recomendamos altamente este manual para todos os interessados nas Ciências da Terra.

Lavinel G, Ionescu, A.A.,B.S., M.S., Ph.D. (Físico-Química/Astrofísica)

"Introdução á Mineralogia Prática" (in Portuguese) treats fundamental concepts necessary for the identification and characterization of minerals and is intended for students of geology, chemistry and related interdisciplinary areas.

The book is well written and includes the updated classification of minerals of the International Mineralogical Association (INA). In a certain way it represents the experience of many years of teaching of the three authors.

It consists of nine chapters, two appendices and seventeen colored plates. It encompasses the geology of mineral deposits, properties of minerals, characterization, taxonomy, classes and subclasses, native elements, industrial uses of and also a description of minerals found in meteorites.

Unfortunately, the colored plates were not inserted in the appropriate places in the text and are poor quality copies of the original photographs of minerals of the Science Museum of the Lutheran University of Brazil (ULBRA) and the Private Collection of Professor Paulo César Pereira das Neves.

Years ago, an Old American Indian Friend from New Mexico - The Land of Enchantment, told us that there are four things in Nature that fascinate mankind with their beauty, radiance and magic. They are the stars, the flowers, the minerals and the sparkling eyes of beautiful women. Apparently the wisdom of some, has not reached others in distant and far away places of Mother Earth, including some editors, more preoccupied with profits and financial aspects.

We recommend the book to students and others interested in the Earth Sciences.

Lavinel G. Ionescu, A.A., B.S., M.S., Ph.D. (Physical Chemistry/Astrophysics)

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CONTRIBUTION TO CO(III) NITROCOMPLEXES CHEMISTRY. NEW ANALOGUES OF $NH_4[CO(NO_2)_4(NH_3)_2]$ COMPLEX WITH HEXAMETHYLENETETRAMINE

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ABSTRACT

The work presents experimental data about new analogues of ammonium tetranitro-diamine Co(III) complex (Erdmann complex) with hexamethyleneteramine (hta). The base complex obtained, $NH_4[Co(NO_2)_4(hta)_2]$, as well as the Erdmann complex, present practical importance for agriculture. They contain nitrogen under cationic, anionic and molecular form and Co(III) as micronutrient and can serve as source of other micronutrients through replacement of NH_4^+ with other complexes cations. Some of these complexes are soluble in water, others are hardly soluble and nonhygroscopic. Their efficiency in fertilizing was demonstrated by us experimentally.

KEYWORDS : Co(III) Nitrocomplexes, Hexamethylenetetramine, Micronutrients

RESUMO

O presente artigo apresenta dados originais obtidos para análogos novos do complexo de amônio e Co(III) com tetranitrodiamina (Complexo de Erdmann) com hexametilenotetramina (hta). O complexo obtido, $NH_4[Co(NO_2)_4(hta)_2]$, bem como o complexo de Erdmann tem importância prática na agricultura. Eles contêm nitrogênio nas formas catiônica, aniônica e molecular e Co(III) como micronutrientes e podem servir como fontes de outros micronutrientes através da troca de NH_4^+ com complexos de outros cátions. Alguns destes complexos são solúveis em água, outros são pouco solúveis e nonigroscópicos. A sua eficiência como fertilizantes foi demonstrada experimentalmente.

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INTRODUCTION

There exists a wide range of complexes of nitroamine [1,2,3] as tetranitro-diamine ammonium Co(III) complex, a compound which was obtained for the first time by Erdmann [2]. This complex can serre as a fertilizer because it contains nitrogen and an element that can be a micronutrient. It has, however some disadvantages, we have extended the Co(III) nitrocomplexes series with fertilizing action to new nitrocomplexes with the general formula $(NH_4)_{n-3}[Co(NO_2)_{6-n}(N_4C_6H_{12})_n]$, where $N_4C_6H_{12}$ is hexamethylenetetramine noted *hta* [2,3] and n has the values of 2 or 3. These complexes are macrocrystalline substances, partially soluble in water, with red or yellow-orange colour. They decompose only at temperature between 138-175°C.

Starting from the base complex with two molecules of *hta* we have obtained a range of other ligands with or without nitrogen and also be replacing NH_4^+ ion with other simple complex ions.

EXPERIMENTAL PROCEDDURE

The procedure of preparing nitrocomplexes that have the general formula mentioned above consisted in treating $CoCl_2 \cdot 6H_2O$ dissolved in distilled water with a solution which contains NH_4Cl, $NaNO_2$ and $N_4C_6H_{12}$ taken in stoichiometrical ratios. The reaction took place in excess NH_4Cl and the oxidation of the reactions mixture is done by bubbling air 1.5 to 2 hours at room temperature. The product is obtained by crystallization for 12-24 hours.

The $NH_4[Co(NO_2)_4(hta)_2]$preparation

The Erdmann analogue preparation was done as follows: A sample of 91.5g $CoCl_2 \cdot 6H_2O$ (0.4mols) was dissolved in 200 mL distilled water which is the first solution and 100 g NH_4Cl (1.8 mols), 110.4 g $NaNO_2$ (1.6 mols) and 112 g $N_4C_6H_{12}$ (0.8 mols) in 1050 mL distilled water which is the second solution. The two solutions were mixed and a clear red with purple blue solution was obtained. The oxidation of the reactions mixture was done by bubbling air for 1.5-2 hours at room temperature. The solution was then allowed to crystallize for 12-24 hours. The reaction is as follows:

$$4CoCl_2 + 8NH_4Cl + 16NaNO_2 + 8N_4C_6H_{12} + O_2 \rightarrow 4NH_3 + 16NaCl + 4NH_4[Co(NO_2)_4(hta)_2] + 2H_2O \quad (1)$$

The nitrocomplex was dissolved in warm water in order to recrystallize it and there was no danger of hydrolyzing. In the case of Erdmann's salt recrystallization was done from a 1M CH_3COOH solution with an efficiency of 91%. The complex obtained has macrocrystals under the form of red bright lamellae of different sizes within regular outlines. It is partially soluble in water (0.23g/100g water at 22°C) and it decomposes at 175°C.

The pentanitro- and trinitrocomplexes preparation with $N_4C_6H_{12}$

Modifying the stoichiometrical ratio between components (increasing $NaNO_2$ quantity and reducing the $N_4C_6H_{12}$ quantity) we obtained the pentanitrocomplex with the formula $(NH_4)_2[Co(NO_2)_5(hta)]$. It presented macrocrystals as bright lamellae with yellow- reddish colour a little different from the one of tetranitrocomplex.

As in the case of Erdmann's salt preparation, excess of $N_4C_6H_{12}$ leads to the formation of the nonelectrolyte form with the formula $[Co(NO_2)_3(hta)_3]$ during the bubbling of air. This is a precipitate with yellow – orange colour, with microcrystals and it is hardly soluble in water.

The three nitrocomplexes, which were obtained with hexamethylenetetramine (hta), were studied using many chemical and physical – chemical methods in order to establish their composition and structure.

The chemical analysis of the complexes

Cobalt was determined by complexonometrical titration using 0.01M complexon III with murexide [4]. For the calculation the following relation was used:

$$Co\% = \frac{0.5894n}{a} x100$$

where *n* is ml complexon used for titration, a is grams substance analyzed and 0.5894 is mg cobalt which corresponds to 1 ml complexon.

The measurement of NH_4^+ ion was done spectrometrically (λ=410 nm) using Nessler reagent. The total nitrogen was determined using the micro-Kjeldahl method. The difference between the total nitrogen and the ammnoniacal nitrogen represents the nitrogen, which is in the complex ion. This make possible to establish the number of NO_2^- groups and complexed *hta* molecules. In the Table 1 are presented the data obtained through chemical analysis for the three-synthetized complexes.

Table 1. The results of the chemical analyses.

Formulae	M_{calc}	η%	Content %					
			Co		NH_4^+		N_{total}	
			Found	Calc.	Found	Calc.	Found.	Calc.
$(NH_4)_2[Co(NO_2)_5(hta)]$	464.93	76.3	12.52	12.67	7.90	7.74	33.01	33.12
$NH_4[Co(NO_2)_4(hta)_2]$	536.93	91.0	10.87	10.97	3.52	3.35	33.70	33.89
$[Co(NO_2)_3(hta)_3]$	616.93	42.5	9.68	9.55	-	-	34.22	34.04

The thermal analysis

Using a Dr. Erdey derivatograph important data were obtained about the composition and the structure of the complexes synthesized. In Figures 1, 2 and 3 the penta-, tetra- and trinitrocomplexes thermograms are presented and in Figure 4 the thermogram of Erdmann's salt is presented.

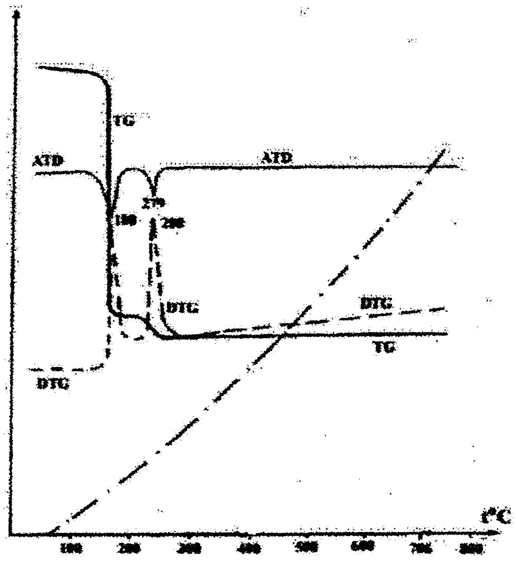


Figure 1. The thermogram of $(NH_4)_2[Co(NO_2)_5(hta)]$

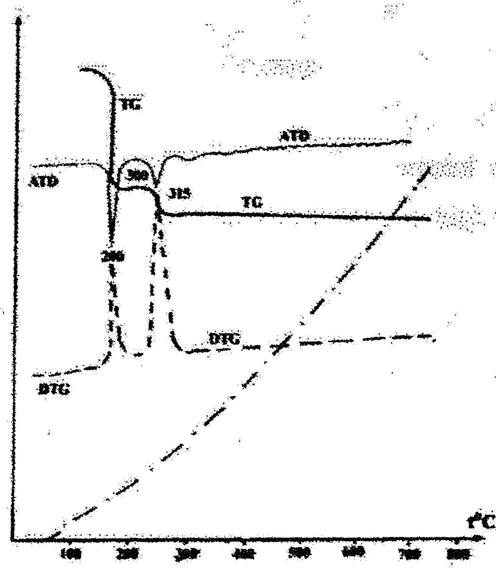


Figure 2. The thermogram of $NH_4[Co(NO_2)_4(hta)_2]$

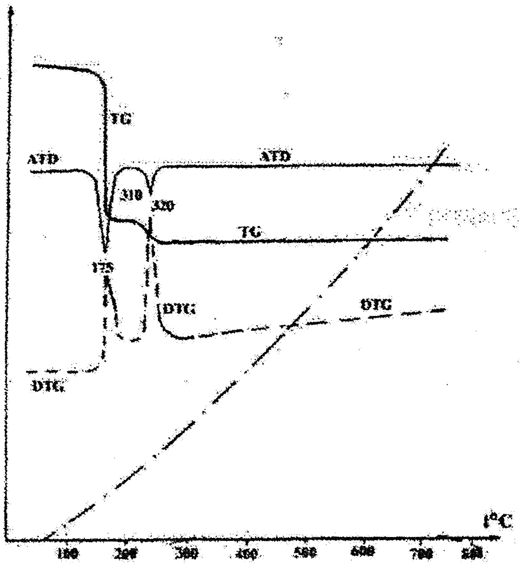


Figure 3. The thermogram of $[Co(NO_2)_3(hta)_3]$

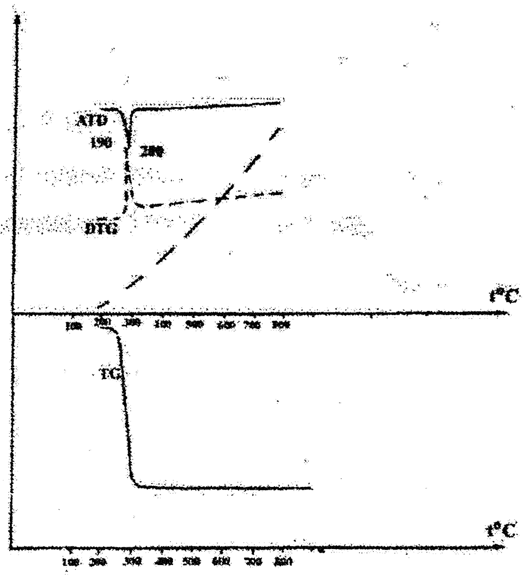


Figure 4. The thermogram of $NH_4[Co(NO_2)_4(NH_3)_2]$

Comparing these thermograms (Figures 1-3) with the thermogram of Erdmann's salt (Figure 4) we notice that:

- the endothermic effect which appears at 175-200°C, for Erdmann's salt, is due to NH_4^+, NH_3 and NO_2^- groups which leave the complex;
- the effect which appears at 275-320°C (Figures 1-3), which is not presented with Erdmann's salt, is due to *hta* which having a higher bond energy, needs a higher temperature in order to leave the complex.

The analysis of the first three thermograms demonstrates that the endothermic effect, which is present because of the chemical bond break between the central ion and *hta*, is bigger than the one produced by of Co-NO_2 bond break. This can be explained both by the strength of bond and by the ligand nature and mass. The ligand with a larger mass and stronger band requires a larger quantity of heat in order to leave the complex. The sharp maximum of DTG curve proves that the effect is produced at a precise temperature (320°C) corresponding to the chemical bond break.

Analyzing the DTG curves of the three new combinations we can show that:
- the first maximum attributed to NO_2^- groups (175-200°C) decreases at the same time with the diminishing number of NO_2^- groups;
- the second maximum from 275 to 320°C, attributed to *hta* groups, increases in temperature and intensity simultaneously with the increase of number of the *hta* molecules.

This is the result of internal interactions, which are bigger when the complex contains more ionic ligands (NO_2^-) than neutral ligands *(hta)*. That is why the Co-NO_2 bond break occurs in the case of pentanitrocomplex at 175°C and the Co-hta bond break takes place at 275°C. In the case of tetranitrocomplex the temperature are higher: 200°C for the Co-NO_2 bond break and 315°C for the Co-hta bond break.

The higher stability of the tetranitrocomplex can also be explained by its octahedral configuration. There are two possible arrangements:
- the two bulky molecules of *hta* at the two tops of the octahedral:
- two NO_2^- ions at the two tops of the octahedral and the other two at the opposite diametrical corners if the base in order to assure a repulsion as small as possible among the NO_2^- ions.

The lamellar structure of pentanitro- and tetranitrocomplex suggests that the second variant is correct. In the case of trinitrocomplex it is not possible to find three bulky groups of *hta* in the base plane. One of the groups is found in one of the octahedral tops. For this reason:
- the macrocrystal lamellar structure disappears and a microcrystal structure appears;
- the solubility decreases;
- the colour is modified from red to yellow as compared to the other two complexes.

The TG curves, which show mass loss varying with temperature, confirm the conclusions drawn from the diagrams ATD and DTG analysis.

The IR spectral analysis

The absorption spectrum in IR of the complexes prepared was recorded with a UR 10 Jenna spectrometer. The tested sample was included into a KBr pellet at a pressure of 80 atm in dilution of 2-10 mg substance / 0.5g KBr. There frequencies were recorded in the range of 400-3600 cm^{-1} (Table 2).

Table 2. The IR spectra of the complexes

Band	$(NH_4)_2[Co(NO_2)_5(hta)]$	$NH_4[Co(NO_2)_4(hta)_2]$	$[Co(NO_2)_3(hta)_3]$
$\delta(NO_2)$	830 s, sh	830 s, sh	830 s, sh
$\nu_{sym.}(NO_2)$	1270 w	1250 w	1230 w
$\nu_{asym.}(NO_2)$	1465 w	1440 w	1420 m
$\gamma(CH_2)$	710 w	710 w	710 w
ν(C-N)	1065 s, sh	1065 s,sh	1065 s,sh
ν(Co-N)(I)	570 w	570 w	570 w
ν(Co-N)(II)	510 w	510 w	510 w
$\nu(NH_4^+)$	3080-3300 w, br	3080-3300 w, br	-

s- strong; w- weak; sh- sharp; m- medium, br- broad
I: Co-N(NO_2); II: Co-N(hta)

From Table 2 it can be noticed that generally with all three complexes there are the same absorption bands but they are shightly shifted and have different intensities. This is because of the resonance state of the atoms, which are fixed in a total correlation with the whole molecular structure, which is different from one substance to anoher.

This explain why the bands at 1270 and 1465 cm^{-1}, which were assigned to the symmetrical and unsymmetrical stretching vibrations of NO_2^- groups [4-6], from the pentanitrocomplex, are shifted ~ 40 cm^{-1} with tetra- and trinitrocomplexes. It can be noticed that the $\delta(NO_2)$ and $\gamma(CH_2)$ vibrations at 830 and 710 cm^{-1} are constant respectively in all three complexes. The C-N stretching vibration characteristic of the C-N bond of *hta* appears at 1065 cm^{-1} and decreases in intensity from pentanitro- to trinitrocomplex.

The Co-N(I) and Co-N(II) stretching vibrations appear in all three complexes at 570 and 510 cm^{-1} respectively. The vibrations at 3080-3300 cm^{-1}, characteristic of NH_4^+ ion, do not appear for the trinitrocomplex, which demonstrates that it is a nonelectrolyte.

The UV spectra

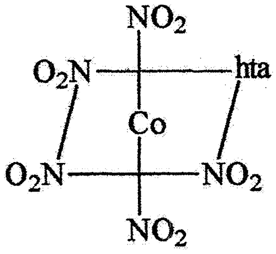
A UNICAM SP 8000 spectrometer was used for recording the absorption spectra in UV. Depending on the number of the NO_2^- and *hta* groups two maxima of absorption were obtained in UV domain.

Analysing these spectra one can notice that the three complexes present the first maximum at 253 nm (with Erdmann's salt λ_1=254 nm) and the second at 350 nm (with Erdmann's salt λ_1=348 nm). From the absorption maxima there were determined the maxim absorbance:

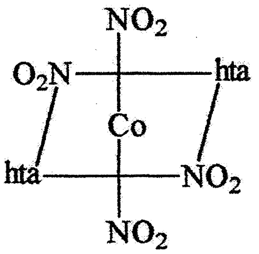
- in the case of pentanitro- and tetranitrocomplexes they are very close (0.30 and 0.33 respectively 0.12 and 0.12);
- in the case of the nonelectrolyte they are very different (0.12 and 50 respectively for the second maximum of absorption);

From the chemical analyses and the other physical-chemical methods which were used we proposed the following structure and the composition of the three nitrocomplexes synthezised:

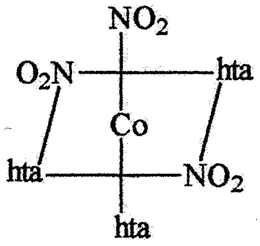
$(NH_4)_2[Co(NO_2)_5(hta)]$



$NH_4[Co(NO_2)_4(hta)_2]$



$[Co(NO_2)_3(hta)_3]$



NEW DERIVATIVES OF $NH_4[Co(NO_2)_4(hta)_2]$

The $NH_4[Co(NO_2)_4(hta)_2]$ complex is an Erdmann analogue as well as all the derivatives resulting from partial or total substitution of *hta* groups. Starting from this base combination we synthetized numerous Erdmann analogues. They contain a useful element for the plant, within the complex ion or they contain instead of the NH_4^+ cation another complexed microelement of the type $[Me(NH_3)_6]^{n+}[Co(NO_2)_4(hta)_2]_n^-$.

Thus, the $NH_4[Co(NO_2)_4(NH_3)(hta)_2]$ complex was studied. It was obtained by introducing into the mixture of reaction both *hta* (according to the stoichiometrical reaction) and NH_3, in small excess. The favourable efficiency was obtained by mixing two solutions as follows:

- the first solution was obtained by dissolving $CoCl_2 \cdot 6H_2O$ (0.4 mols) in 200 mL distilled water;
- the second solution by dissolving NH_4Cl (1.8 mols), *hta* (0.4 mols), $NaNO_2$ (2 mols) and NH_3 25% (2 mL) in 950 mL distilled water;

Air was bubbled in the two solutions for 2 hours after mixing. The purple colour of the solution becomes red and it is turbid because the nonelectrolyte $[Co(NO_2)_3(hta)_3]$ is formed in a small quantity. It need 2-3 days for crystallizing after filtering. Crystals with bright red lamellae are obtained. The chemical and physical-chemical studies confirm the $NH_4[Co(NO_2)_4(NH_3)(hta)]$ complex composition and structure. The fact that the Erdmann salt does not appear even in traces (it can be seen with naked eye), because it has dark-brown prismatic crystals, proves that *hta* as a ligand a higher affinity for cobalt than for NH_3. The IR spectrum of this complex confirms the presence of the NH_3 groups by the presence of the weak band at 1620 cm^{-1} (δ_{asym} NH_3 vibrations) [7-9] and the band at 1310 cm^{-1} (δ_{sym} NH_3 vibrations).

In the same way we obtained new derivatives, which contain, another ligand ion or molecule in the complex ion besides the four NO_2^- groups and one *hta* molecule. The formula of the new complex ion is $[Co(NO_2)_4(hta)X]^-$ where W is the new ligand which is introduced by synthesis [10-13].

Table 3 presents examples of such derivatives, which are considered Erdmann's analogues. In the same table are presented analogues, which are obtained by replacing the NH_4^+ cation with metallic cations such as Ag^+, Hg_2^{2+} and Tl^+. They are obtained by a simple precipitation of $[Co(NO_2)_4(hta)X]^-$ ion with the metal salts or with ammonia complex cations or derivatives [14-16].

Table 3. New analogues of $NH_4[Co(NO_2)_4(hta)]$

Complex combination	M (calculated)	η%	Aspect	Co(III)%	
				Calculated	Found
$NH_4[Co(NO_2)_4(hta)(SCN)]$	476.93	68.20	irregular plates, microcrystals, pink-lilas coloured	12.35	12.5
$NH_4[Co(NO_2)_4(hta)(py)]$	480.03	71.10	rhombic plates macrocrystals, pink coloured	12.27	12.38
$Ag[Co(NO_2)_4(hta)(NH_3)]$	507.83	*	plates microcrystals, dark-yellow coloured	11.60	11.32
$Hg_2[Co(NO_2)_4(hta)(NH_3)]_2$	1201.04	*	plates microcrystals, reddish coloured	4.91	5.18
$Tl[Co(NO_2)_4(hta)(NH_3)]$	604.3	*	plates microcrystals, dark-yellow coloured	9.75	9.60
$(NH_4)_2[Co(NO_2)_4(hta)(CN)]$	444.93	64.50	irregular plates microcrystals, red-brick coloured	13.24	13.11
$[Cu(NH_3)_4]A_2$	931.41	*	plates microcrystals, greenish coloured	6.33	5.98
$[Zn(NH_3)_4]A_2$	933.23	*	plates microcrystals, yellow-golden coloured	6.31	6.14
$[Co^{III}(NH_3)_4(CO_3)]A$	586.86	*	plates macrocrystals, brown coloured	10.04	10.41
$[Co^{III}(NH_3)_4(C_2O_4)]A$	702.86	*	plates macrocrystals, chocolate coloured	8.38	8.02

*- total precipitating; $A=[Co(NO_2)_4(hta)(NH_3)]$

The latter compounds are hardly soluble and they have different colours due to the presence of the second complexed metal which could be used as a microelement for fertilizing plants.

CONCLUSIONS

The Erdmann complex presents properties of fertilizing plants because it contains both nitrogen under different forms and Co(III) as a microelement. But this combination has many disadvantages for use. Among them we mention: decomposing under action of light and unstable character in water solution.

The analogue obtained by us, $NH_4[Co(NO_2)_4(hta)_2]$, eliminates these disadvantages because *hta* is tied more strongly to Co(III) and has a higher stability. The paper presents the way for obtaining and studying the composition and structure of the above mentioned analogue and a number of other derivatives. The general formula of the complex ion is $[Co(NO_2)_4(hta)X]^-$ and its charge is neutralized by monovalent metallic cations or complex ions.

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THE HEAVY METAL COPPER IN THE SEWAGE SLUDGE OF MARINGÁ, PR, BRAZIL

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ABSTRACT

Human wastes are a permanent challenge to the environment. Current research has evaluated the amount of copper metal in the sewerage and in the sludge of the Sewerage Treatment Stations (STSs) of Maringá PR Brazil. Sample collection was undertaken at the STSs and samples were digested with nitric acid at reduced volume. Biosolid samples, previously dried and ground, at constant weights, were digested by aqua regia. Determination of metal concentrations was made by atomic absorption spectrometry. The pH, nitrogen, carbon and organic matter (OM) values were determined by the respective classical methods. Total average were: a) Cu in affluent sewerage 0.077 and effluent sewerage 0.058 $\mu g\ mL^{-1}$. *b) biosolid: Cu = 0.74* $mg\ g^{-1}$*; pH = 3.38; N = 3.24 %; C = 24.5 % e OM = 42.1 %. Variance analysis of the experimental values, and taking into consideration the variation sources of STSs and collection time, showed that no significant difference between the values of copper concentration, N (%), C (%) and organic matter (%) respectively existed in both variation sources. Total average rate of copper concentration of STSs is higher than the international world average value found in the relating literature. Amounts of organic matter and the C:N (carbon:nitrogen) proportions of sewage sludge are appropriate for soil application.*

Key words: sewerage, biosolid, heavy metals, nutrients, environmental pollution, organic matter.

RESUMO

Os resíduos da ação antrópica são um permanente desafio ambiental. Neste sentido, este trabalho teve como objetivo avaliar o metal pesado Cu no esgoto e lodo das ETEs de Maringá. As amostras de esgoto foram digeridas em meio ácido nítrico com redução de volume, as de biossólido foram digeridas com água régia. As leituras das concentrações de cobre foram feitas pelo método de espectrometria de absorção atômica. O pH, o N e o C foram determinados pelos respectivos métodos clássicos. Os resultados em valor médio global foram os seguintes, respectivamente: a) Cu em $\mu g\ mL^{-1}$, *para o esgoto afluente 0,077 e para o esgoto efluente 0,058. b) para o biossólido: Cu = 0,74* $mg\ g^{-1}$*; pH = 3,38; N = 3,24 %; C = 24,5 % e MO = 42,1 %. Pelos resultados conclui-se que, o esgoto efluente está conforme a legislação e o lodo das ETEs: apresenta valores médios de pH; concentração de cobre, N, C e MO, que, em nível de 5%, não têm diferença significativa entre si, tanto nas estações de tratamento quanto no tempo das coletas, respectivamente. O biossólido apresenta um valor médio global de cobre mais elevado que o apresentado por lodos de esgoto em nível internacional. O teor de matéria orgânica e as relações C:N dos lodos das três ETEs são recomendáveis para o uso agrícola.*

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INTRODUCTION

Human society produce a type of refuse, the result of daily activities, which may be called urban residue or waste [1,2]. Home sewage, the type of waste proper to urban centers, is frequently placed untreated in the environment, endangering water sources, health, the environment and the quality of life[3].

For centuries man has been aware of the relationship between poor health situations and public health problems. As far as 1840, owing to fear of epidemics, European communities have made mandatory the application of technologies in waste and sewage treatment. They started to dispose sewage in the soil and drastically reduced epidemic-caused mortality[4].

Treatment of urban sewage produces sewage sludge whose final disposition is highly problematic for Sewerage Treatment Stations (STSs). Without previous analysis of its physical, chemical and biological composition, inadequate disposition of untreated sewage sludge may pollute the soil and water sources. It may also alter their physical, chemical and biological characteristics, besides being an aesthetic problem and, worse still, a threat to the environment and public health[5, 6].

Since copper is a heavy metal[7], it has been and still is very important in the development of civilization and in the recent past has been among the five metals most used in the world[8]. Copper may be found naturally (Cu) and as a mineral, cuprite [Cu_2O], malachite [$Cu_2(CO_3)(OH)_2$], chalcosite [Cu_2S], chalcopyrite [$CuFeS_2$], azurite [$Cu_3(CO_3)(OH)_2$], and others[9]. Mean rate of copper in rocks of the earth's crust is close to 55 $\mu g\ g^{-1}$ [10]. Since copper is relatively available and movable in the soil[11], it has variable concentrations in the latter, frequently at toxic rates for biota[12]. It is also a contaminating element carried through the air[13] and in water[14]. In the largest rivers it is found at interval rates of 0.830 - 152 $\mu g\ L^{-1}$ [15, 16, 17].

Several copper derivatives are toxic and even highly toxic[18]. Although used as a fungicide in vineyards and coffee plantations[19], it is one of the micronutrients necessary for animal and vegetative life[20]. Actually its presence in protein and enzymes makes it an essential element[21].

Decree No. 20 of the Brazilian Council for the Environment (CONAMA), published in June 1986, reads that a disposable effluent, such as the case of treated sewage sludge, should contain a maximum copper concentration rate of 1 $mg\ L^{-1}$. In the case of fresh water maximum concentration limits recommended are 20 $\mu g\ L^{-1}$ (Class 1 and 2 water) and 50 $\mu g\ L^{-1}$ (Class 3 and 4 water)[22].

Although several dispositions, among which may be mentioned its application in the soil, have been conjured up for the biosolid, none is completely safe. As a general rule, sludge is rich in organic matter, nitrogen, phosphorus and micronutrients and its use as a fertilizer in agriculture has great advantages[23, 24, 25, 26]. However, risks exist, particularly those proper to heavy metals and pathogenic agents[27].

Several studies have been undertaken on the application of sewage sludge in agriculture. The problem has been tackled from several angles especially on the mineralization and the availability of nutrients[28, 29, 30, 31], absorption of ions made available by plants[32], production yield of vegetations[33, 34, 35].

Owing to possible environmental impacts caused by the application of sewage sludge, studies have been undertaken not only at international[26] and national[23] levels to establish usage criteria[23]. Even the state of Paraná has tackled the problem[24].

Recycling of sewage sludge in agriculture is a natural trend worldwide, as may be surmised from the themes and conferences given at the I Mercosur Seminar on Administration of Biosolids[36]. In the wake of analyzing sludge application, current research is concerned with copper, which has been used for many years and in still used in the Maringá region as a fungicide in vineyards and on coffee shrubs[37, 38]. There has surely been an accumulation of the heavy metal in the environment during so many years of usage. In spite of the fact that copper concentration dilutes in natural systems, it may reach urban sewage through food and the water system. Concern with the sewage sludge at such concentrations and rates is becoming high.

The present research evaluates the concentration of the heavy metal copper in sewage and in sewage sludge of the Sewerage Treatment Stations of Maringá (STS-1, STS-2 and STS-3).

MATERIALS AND METHODS

Biosolid: collection and first preparation of samples

Sewage treatment in Maringá is done by anaerobic reactors (Anaerobic Reactor of Fluidized Sludge, RALF). Samples of sludge were collected by technicians of the Water Works Department of the state of Paraná (SANEPAR) at STS-1, STS-2 and STS-3.

At the lab sludge samples were dried at room temperature, ground, sieved and taken to a 60°C buffer till they reached constant weight. They were then stored in polyethylene bags for analysis.

Biosolid: analysis of the heavy metal

A mass of dry sludge, weight 2.0000 g, was transferred to a 125-mL Erlenmeyer glass with emery rim. 2 to 3 mL of distilled and de-ionized water were added to the mass to make it turn into paste. Aliquots of 7.5 mL of concentrated chloridic acid and 2.5 mL of concentrated nitric acid were added for each gram of sludge. Flasks were covered and left to rest during a 12-hour period, at night, at room temperature. Flasks were then heated in a 40cm-high reflux condenser system, during 2 hours. Solution of digested matter was filtered and collected in a 100-mL volumetric balloon. Care was taken to wash the condenser, Erlenmeyer glass and the filter paper and residue with portions of nitric acid 2 mol L^{-1} [39]. Control and analytic curve standards underwent the same process. Determinations of copper concentrations were done by atomic absorption spectrometer Varian, model Spectr AA 10 PLUS, flame mode[40]. Method had a detection limit of (c_L) = 0.027 µg mL^{1-}, with 99% confidence level[41].

Biosolid: analysis of organic matter

A sample of 30.0 mg of dry sludge was transferred to a 250-mL Erlenmeyer glass; 10mL of potassium dichromate 0.1667 mol L^{-1} and 20mL of concentrated sulfuric acid were added respectively; solution was shaken well and left to rest for 20 – 30 minutes. It was then diluted to 100 mL with distilled and de-ionized water; 3 to 4 drops of ortho-phenanthroline were added and completed with hexahydrated ferrous sulfate 1.0 mol L^{-1}. Percentage of C determined the percentage of organic matter[42].

Biosolid: analysis of total nitrogen

After 0.1000 g of the sample has been placed in each 25x250mm-glass tube, 1 mL of H_2O_2 at 30% and 3 mL of concentrated sulfuric acid were added and left to cool for 15-20 minutes. Afterwards, 0.7 g of digesting mixture were added and flasks were taken to the digester SARGE, temperature was raised every 15 min till it reached 330°C and maintained for 2 h. After cooling, the samples were placed in flasks for distillation of NH_3, with 30 mL of de-ionized water and 30 mL of NaOH at 40%. Condensed vapors of NH_3 were collected in 10 mL of boric acid with indicator. After collecting 30 to 35 mL of the distilled solution, it was completed with sulfuric acid 0.05 mol L^{-1} [43].

Biosolid: pH

Determination of pH was undertaken as from 15 mL of dry sample in a test-tube and placed in a 125-mL Erlenmeyer glass. Aliquot of 25 mL de-ionized water were then added[44], the mixture was shaken, and the pH of supernatant was measured by a pH-meter after decantation.

Sewage: collection and initial preparation of samples[45]

Sewage samples were also collected by technicians of the Water Works Department – Maringá Section, at STS-1, STS-2 and STS-3. Two liters of the compound sample of affluent sewage that arrived at each STS and 2 liters of compound sample of effluent sewage that came out of each STS were stored in clean plastic flasks[46, 47], and preserved at $pH<2$ by adding concentrated HNO_3. They were stored at 3 °C till the respective analyses, which were done immediately[48, 49].

Sewage: digestion of samples and analysis of the metal

Samples were prepared to calculate total concentration of copper. After homogenization of the sample, 500 mL of each sample were transferred to their respective beakers, labeled and covered with glass, in duplicate, and 5 mL of concentrated HNO_3 were added. The solution was slowly warmed till almost dried and repletion was done when necessary so that sample could be digested. Residue was dissolved by portions of the HCl 5 mol L^{-1} solution, and transferred to a 50-mL volumetric flask with distilled and de-ionized water till completion of marked volume. The sewage sample was thus ready for copper concentration contents.

Copper concentrations were read by atomic absorption spectrometer Varian, Spectr AA 10 Plus model, flame mode, according to recommendations by Handbook and by Welz and Sperling[40]. Although the method's detection limit (c_L) was 0.027 µg mL^{-1}, samples were concentrated ten times (500 mL of in natura sample were reduced to 50 mL of prepared solution). This means that the sample of the original sewage, concentration 0.0027 µg mL^{-1}, would produce an analytic signal of the sample at 99% reliability after a 10 fold concentration. Sewage with copper concentrations less than

0.0027 μg mL^{-1}, done with the same technique, would not produce any reading analytic signal.

Statistical analysis

Results underwent variance analysis and Tukey's test with SANEST.

RESULTS AND DISCUSSION

Sewage

SANEPAR-Maringá Technical Data (1997)[50] shows that the sewage system in Maringá is formed by three basins. Main basins direct the collected sewage to STS-1, STS-2 and STS-3 operating with anaerobic reactor systems of fluidized sludge (RALF).

Sludge from the south basin is collected by STS-2 which services downtown Maringá, the old districts (zones 2, 3, 4 and 5) and the most recent districts close to the above.

The northern region has two big basins. Both concentrate the sewage from STS involving Maringá Stream (STS-1) and the other involving Morangueira Stream (STS-3).

Sewage treatment in Maringá is based on the anaerobic stabilization process of organic matter. Pre- and first treatments are traditional, whereas the second treatment is done by Anaerobic Reactors of Fluidized Sludge (Figure 1).

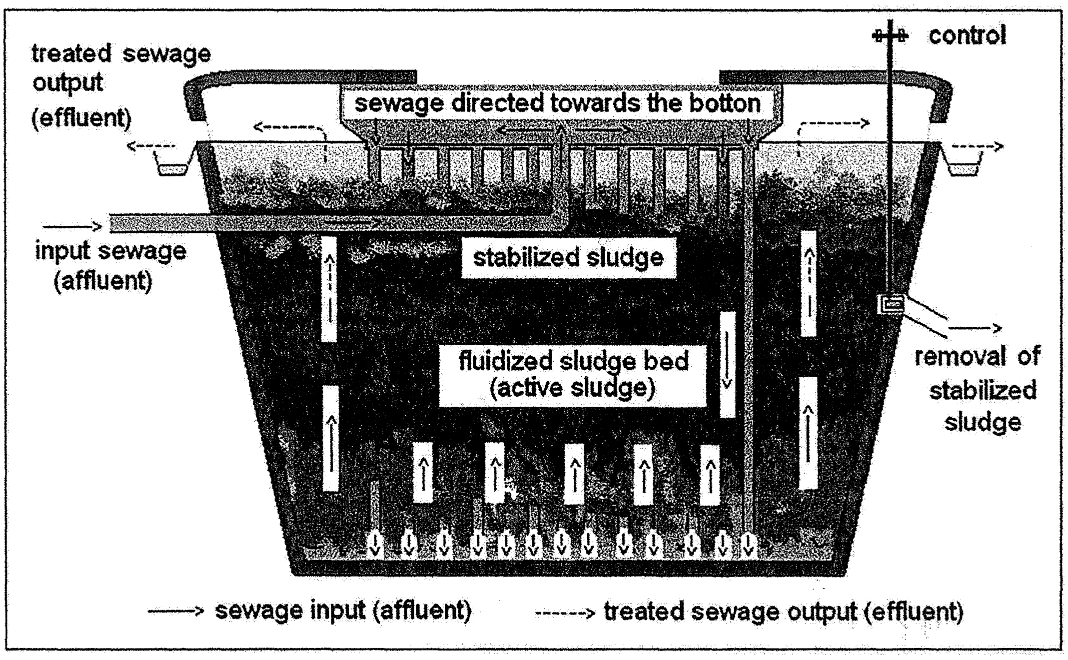

Figura 1. Cross-section and processing of an Anaerobic Reactor of Fluidized Bed (RALF)[52].

Figure 1 shows that no air (or oxygen) exists in the descent of sewage to the reactor's bottom. Oxygen in the fluidized sludge is practically zero, or rather, a hypoxia environment is created which may be called anoxia due to the complete lack of oxygen. Chemical species in this environment are reduced to a minimum, or rather, to an environment with electron availability, called a reducing environment. Two factors may explain this: (a) the lack of the oxidant agent oxygen; (b) the biota in this environment causes fermentation [1] in its quest for energy and a reduction reaction[51] too.

$$2\ \underset{\text{biomass}}{|CH_2O|} \xrightarrow[\text{organisms}]{\text{anaerobic}} \underset{\text{Methane}}{CH_4} + CO_2 + \text{Energy} \qquad [1]$$

Equation [1] shows reaction with two stages, given in [2] and [3] which, when added together, reproduce equation [1]. In the two reactions, oxidation status was indicated (in Arabic numerals) for the key element involved in the oxidation-reduction reaction, on the upper right side.

1st Stage

$$2.\underset{\text{biomass}}{|C^{(0)}H_2O|} + 2.H_2O \xrightarrow[\text{organisms}]{\text{anaerobic}} 2.C^{(4+)}O_{2(g)} + 8.H^{+} + 8.\mathbf{e} \qquad [2]$$

2nd Stage

$$C^{(4+)}O_{2(g)} + 4.H^{+} + 8.\mathbf{e} \xrightarrow[\text{organisms}]{\text{anaerobic}} \underset{\text{methane}}{C^{(4-)}H_4} + 2.H_2O \qquad [3]$$

$$2.\underset{\text{biomass}}{|C^{(0)}H_2O|} \xrightarrow[\text{organisms}]{\text{anaerobic}} \underset{\text{methane}}{C^{(4-)}H_4} + C^{(4+)}O_2 + \text{Energy} \qquad [1]$$

Reduction reactions are processed in the fluidized bed of the reactor (Figure 1) and may be perceived in stage [2] in which 8 electrons are released by fermentation. This is due to the passing of carbon from the biomass's oxidation status 0 (C^{o}) to carbon with oxidation status 4+ (C^{4+}) of CO_2. Released electrons of the latter may also reduce other species, such as CO_2 to CH_4, in which C^{4+} of CO_2 becomes C^{4-} in CH_4. In the case of other species, sulfate (SO_4^{2-}, with S^{6+}) [4] releases hydrogen sulfide gas (H_2S, with S^{2-}) causing the bad smell.

$$\underset{\text{Sulfate}}{SO_{4\,(aq)}^{2-}} + 2\ \underset{\text{biomass}}{|C^{(0)}H_2O|} + 2\,H^{+} \xrightarrow[\text{organisms}]{\text{anaerobic}} \underset{\text{Hydrogen sulfide}}{H_2S_{(g)}} + 2\,CO_2 + 2\,H_2O \qquad [4]$$

It may be observed that in anaerobic processes, or rather, those that occur in the absence of air, albeit with oxygen, there is a 'release' or an 'availability of electrons' in the environment. The latter becomes a reducing environment with greater electronic activity.

Table 1 shows analytic results of mean concentrations of copper in the sewage input at the STS (affluent sewage) and the sewage output from the STS (effluent sewage), in each unit and total averages.

Total data of Table 1 show that the interval in mean concentrations, in µg mL^{-1}, in input sewage of all STSs is $(0.40–45.8)10^{-2}$, mean rate 0.0773, whereas that in output sewage of all STSs is $(0.40-56.4)10^{-2}$, mean rate 0.0576.

Table 1 shows a 25.5% retention of copper in STSs when total averages of Cu input and output are compared. Consequently, STSs are efficient in copper retention, which will be found in the sewage sludge.

Table 2 shows variance analysis of copper concentrations in sewage input of the place (3 STSs) and time (collection period), analyzing the phenomenon's temporality, as variation sources, with possible significant difference. Experimental results fail to give any significant difference, at 5% level, between copper concentration rates that arrive at STSs.

Table 1. Efficiency Evaluation of STS of Maringá in Retention of Copper (Cu).

		STS - 1		STS - 2		STS - 3	
Month	Year	Input (µg mL^{-1})	Output (µg mL^{-1})	Input (µg mL^{-1})	Output (µg mL^{-1})	Input (µg mL^{-1})	Output (µg mL^{-1})
Sept	1999	$5.70x10^{-2}$	$2.70x10^{-2}$	$6.90x10^{-2}$	$3.20x10^{-2}$	$4.00x10^{-2}$	$1.20x10^{-2}$
Oct	1999	$7.20x10^{-2}$	$2.40x10^{-2}$	$7.70x10^{-2}$	$3.20x10^{-2}$	$3.50x10^{-2}$	$2.80x10^{-2}$
Nov	1999	$4.40x10^{-2}$	$2.20x10^{-2}$	$7.30x10^{-2}$	$4.00x10^{-2}$	$4.70x10^{-2}$	$2.20x10^{-2}$
Jan	2000	$4.80x10^{-2}$	$1.50x10^{-2}$	$3.10x10^{-2}$	$2.70x10^{-2}$	$5.80x10^{-2}$	$2.70x10^{-2}$
Mar	2000	$2.70x10^{-2}$	$2.70x10^{-2}$	$4.20x10^{-2}$	$2.70x10^{-2}$	$4.10x10^{-2}$	$1.20x10^{-2}$
May	2000	$2.90x10^{-2}$	$0.40x10^{-2}$	$0.90x10^{-2}$	$2.60x10^{-2}$	$2.40x10^{-2}$	$1.70x10^{-2}$
Aug	2000	$36.5x10^{-2}$	$6.50x10^{-2}$	$2.20x10^{-2}$	$2.00x10^{-2}$	$10.9x10^{-2}$	$2.10x10^{-2}$
Oct	2000	$15.5x10^{-2}$	$56.4x10^{-2}$	$45.8x10^{-2}$	$20.5x10^{-2}$	$12.4x10^{-2}$	$23.9x10^{-2}$
May	2001	$0.90x10^{-2}$	$0.80x10^{-2}$	$1.80x10^{-2}$	$0.40x10^{-2}$	$0.40x10^{-2}$	$0.80x10^{-2}$
Data for STS							
Interval:		0.0090-0.365	0.0040-0.564	0.0090-0.458	0.0040-0.205	0.0040-0.124	0.0080-0.239
Mean:		$8.95x10^{-2}$	$8.40x10^{-2}$	$8.88x10^{-2}$	$4.59x10^{-2}$	$5.36x10^{-2}$	$4.29x10^{-2}$
Standard Deviation:		$11.1x10^{-2}$	$18.1x10^{-2}$	$14.1x10^{-2}$	$6.05x10^{-2}$	$3.89x10^{-2}$	$7.39x10^{-2}$
Median:		$4.80x10^{-2}$	$2.40x10^{-2}$	$4.20x10^{-2}$	$2.70x10^{-2}$	$4.10x10^{-2}$	$2.10x10^{-2}$

Total Data	Input	Output
Total Interval:	$(0.40-45.8) x10^{-2}$	$(0.40-56.4) x10^{-2}$
Mean ±s:	$(7.73\pm10.1) x10^{-2}$	$(5.76\pm11.5) x10^{-2}$
Median:	$4.40x10^{-2}$	$2.60x10^{-2}$

STS-1 – Sewage Treatment Station in the districts of Mandacaru, Jardim Universitário and Zone 7; STS-2 – Sewage Treatment Station of South Region (central region, zones 2, 3, 4, 5 and new districts of Maringá); STS-3 – Sewage Treatment Station of districts Jardim Alvorada and Ribeirão Morangueira, s – Standard Deviation. Note: concentration rates lower than the Limit of Detection (c_L = 0.0027 µg.mL^{-1}) were maintained for statistical calculations since there may be a 1% chance of being verified.

Results seem to show that, at 5% significance level, no dangerous refuse containing copper occurred in the sewage network during this specific period.

Art. 21 of Law 20/1986 of the CONAMA reads:

> Effluents from any polluting source may be released directly or indirectly into water sources under the conditions below:

g) maximum rates permitted of the following compounds: Cadmium, 0.2 mg L^{-1}; Lead, 0.5 mg L^{-1}; Copper, 1.0 mg L^{-1}; Hexavalent Chromium, 0.5 mg L^{-1}; Trivalent, 2.0 mg L^{-1}; Soluble iron, 15.0 mg L^{-1}; Manganese, 1.0 mg L^{-1} and Zinc, 5.0 mg L^{-1}.

Effluent from STSs lies within the legal conditions of the above law when the highest interval value (0.564 μg mL^{-1}) for copper are taken into consideration.

When average and higher interval values of output concentrations of some metals into the environment are analyzed, it may be seen that they are below the limits established by CONAMA. Table 3 shows that, since rates are within the CONAMA limits, the respective effluents may be deposited into the environment.

Table 2. Data Variance Analysis of Mean Values of Copper Concentrations in the Affluent Sewage to STS of in μg mL^{-1}.

Causes of variation	F.D.	S.S.	M.S.	Rate of F	Prob > F
Place	2	76.1163	38.0581	0.4799	0.63241
Time	8	1430.7162	178.8395	2.2549	0.07901
Residue	16	1268.9837	79.3115		
Total	26	2775.8162			

General Mean = $7.73.10^{-2}$
Variation Coefficient = 115.215 %

F.D. – Freedom Degree; S.S. – Sum of Squares; M. S. – Mean Square; $F_{place} = \sigma^2_{(place)}/\sigma^2_{(Residue)}$ e $F_{Time} = \sigma^2_{(Time)}/\sigma^2_{(Residue)}$.

Table 3. Total Mean Concentrations of Some Metals in the Affluent and Effluent Sewage of STSs of Maringá and Their Respective Sewage Sludge in the Period 1999–2000.

Metal	Total Metal Concentration of Metals from STS-1, STS-2 and STS-3				
	Sewage				Sewage
	Affluent Sewage from STSs		Effluent Sewage from STSs		
	Mean (μg mL^{-1})	Interval (μg mL^{-1})	Mean (μg mL^{-1})	Interval (μg mL^{-1})	sludge (μg g^{-1})
Cu	0.091	0.0040-0.46	0.058	0.0040-0.56	410.9
Pb	0.089	0.0060-0.46	0.070	0.020-0.13	357.7
Zn	0.25	n.d. – 0.62	0.17	n.d. –0.69	1,517
Mn	0.11	0.055-0.22	0.10	0.060-0.17	144.8
Fe	2.87	0.22-9.88	2.20	0.11-6.77	53,066
Cd	n.d.	n.d – 0.0080	n.d	n.d – 0.0020	
					2.74
Cr	0.0057	n.d. – 0.037	0.0059	n.d. – 0.037	67.5

STS-1 – Sewage Treatment Station of districts Mandacaru, Jardim Universitário and Zone 7; STS-2 – Sewage Treatment Stations of South region (central region, zones 2, 3, 4, 5 and new districts in Maringá); STS-3 – Sewage Treatment Station of districts Jardim Alvorada and Ribeirão Morangueira. n.d. – not detected by method, concentration less than Detection Limit (c_L).

Sewage sludge (or biosolid)

After a certain period, varying between 2 to 4 months, depending on the physical, biological, physical and chemical characteristics of the reactor, non-consumed organic matter (OM) is stabilized (Figure 1). It turns into particled flakes that make up the sewage sludge or biosolid, which is removed from the reactor as 'fluid material'. Or rather, organic matter dispersed in water with many lyophilic chemical groups. It is generally spread in a thin film on protected soil surfaces and then left to dry or to release most of its water. The sewage sludge is actually the solid with particle agglomerates.

Table 4 shows pH values, mean concentration values of copper per STS, and total rate of copper concentration (0.74 mg g^{-1}) from August 1997 to March 2000.

Table 4. Concentration of Heavy Metal Copper in Sewage of Sewage Treatment Stations (STS) of Maringá.

Sample (n.)	Month and Year	STS-1 pH	STS-1 Cu (mg g^{-1})	STS-2 pH	STS-2 Cu (mg g^{-1})	STS-3 pH	STS-3 Cu (mg g^{-1})
1	08.97	3.29	0.35	4.40	1.66	3.25	1.57
2	11.97	4.01	0.32	3.30	0.59	3.90	1.09
3	03.98	3.43	0.51	3.45	0.61	3.15	3.71
4	05.98	3.73	0.60	4.15	0.92	3.67	1.42
5	06.98	3.56	0.48	3.06	0.68	2.89	0.53
6	08.98	3.32	0.33	3.41	0.87	2.82	0.14
7	10.99	3.45	0.45	3.06	0.51	2.92	0.27
8	01.00	3.56	0.30	3.26	0.40	2.72	0.19
9	03.00	3.67	0.55	3.10	0.62	2.80	0.40
Mean ±s:		3.56	0.43	3.47	0.76 ±0.37	3.12	1.04 ±1.14
Intervals:		3.29-	0.30-0.61	3.06-4.40	0.40-1.66	2.72-3.90	0.19-1.57

Total Rates of 3 STSs

	Copper (mg g^{-1})	pH
Mean ±s:	0.74 ±0.70	3.38 ±0.41
Interval:	0.19 – 1.66	2.72 – 4.40

STS-1 – Sewage Treatment Station of districts Mandacaru, Jardim Universitário and Zone 7; STS-2 – Sewage Treatment Station of South region (central region, zones 2, 3, 4, 5 and new districts of Maringá); STS-3 – Sewage Treatment Station of districts Jardim Alvorada and Ribeirão Morangueira; s – standard deviation; analyses were done in triples.

Table 5 shows the variance analysis of results of copper concentration in the biosolid with two possible causes for variation: place (STSs) and time (sampling period) that reveals the phenomenon's temporality. No significant difference exists, at 5% variance analysis, between copper concentrations of the three STSs, throughout the collection period.

Table 6 exhibits mean world rate and the respective rate interval of heavy metals for sewage sludge and for arable soil. Sewage sludge in Maringá (Table 4) has 7.2%

copper more than mean world rate and 66.0% higher with regard to mean interval rates. This copper rate has already been detected in STS-2[53] and in STS-2 and STS-3[54].

Since sewage sludge is a sewage residue, indirectly revealing the composition of water, food, environmental refuse, human behavior and others, it seems that copper concentration has been caused by fungicides on coffee shrubs[37, 38] and vines. In fact, the region of Maringá has been a large coffee plantation for many years in which copper fungicides were extensively used, similarly to what happens at present with regard to vineyards in the same region. Further, RALF process of the STSs retains 25.5% of the copper input from home sewage. It seems, therefore, that the high rate is due to copper use as an agricultural defense factor in the entire region, confirming Lavoisier's law that in Nature nothing is lost, nothing is created, but everything is transformed.

Table 5. Variance Analysis of Data for Mean Rates of Copper Concentrations in Sewage Sludge of STS in Maringá, in mg g^{-1}.

Causes of variation	F.D.	S.S.	M.S.	Rate of F	Prob > F
Place	2	1.643	0.821	1.856	0.187
Time	8	4.485	0.561	1.267	0.326
Residue	16	7.082	0.443		
Total	26	13.210			
General Mean = 0.74 mg g^{-1}					

F.D. – Freedom Degree; S.S. – Sum of Squares; M. S. – Mean Square; $F_{Place} = \sigma^2_{(Place)}/\sigma^2_{(Residue)}$ and $F_{Time} = \sigma^2_{(Time)}/\sigma^2_{(Residue)}$.

Table 6. Mean Concentrations and Interval Concentrations of Metals in the Soil and in Sewage Sludge in World Level, and in Acceptable Maximum Concentrations, AMC*,[12] in agricultural soil, in the literature.

Metal	Type of material	Mean (μg g^{-1})[11]	Interval of rates (μg g^{-1})[11]	Interval of rates (μg g^{-1})[56]	AMC[12] (μg g^{-1})	
					Interval[12]	Median
Cu	Sludge	690	100 – 1,000	...	...	
	Soil	30	2.0 - 250	6.0 - 80	23 – 140	100
Zn	Sludge	2,250	1,000 – 10,000	...	...	
	Soil	90	1.0 - 900	17 - 125	70 - 400	265
Mn	Sludge	1,980	60 – 3,600	...	...	
	Soil	1,000	20 – 10,000	80 – 1,300	1,500-3,000	1,500
Pb	Sludge	1,832	136 – 7,627	...	...	
	Soil	20	2.0 - 200	10 - 84	20 - 500	100
Cr	Sludge	1,221	20 – 40,615	...	...	
	Soil	40	10 - 150	7 - 221	50 - 600	100
Cd	Sludge	74	2.0 – 1,100	...	...	
	Soil	0.35	0.010 – 2.0	0.060 – 1.1	3.0 – 8.0	3.0

* - Acceptable Maximum Concentrations, terminology by KABATA-PENDIAS, PENDIAS (1992)[12]; ... – non-calculated rates by authors above.

Mean pH values of sludge in STS-1, STS-2 and STS-3 may be found in Table 4. Total averages of each STS are 3.56; 3.47 and 3.12 respectively, with 3.38 as total average. There is no significant difference in average rates of the three STSs throughout the sampling period, according to variance analysis and Tukey's test, at 5% significance level. Low pH rates are favorable for the release of copper.

Since biosolids are applied to agriculture, relationship C:N and rate of organic matter, given by the product of (% of C) x 1.72[55] (Table 7), were also analyzed.

Table 7 shows concentration rates of organic matter in the 3 STSs which lie within the interval between 28.0% and 55.6%, with 42.1% as total average. There is no significant difference, at 5% level, between rates for STSs and periods of sludge collection.

Table 7. Ratio C:N and Organic Matter (OM) in sludge of the Sewage Treatment Stations (STSs) of Maringá.

	STS-1			STS-2			STS-3		
(Sample) Month/Year	N (%)	C (%)	C:N	N (%)	C (%)	C:N	N (%)	C (%)	C:N
(1) 08/97	2.44	19.1	**8:1**	3.26	32.3	**10:1**	3.35	24.8	**7:1**
(2) 11/97	3.64	27.7	**8:1**	2.40	22.6	**10:1**	3.08	22.7	**7:1**
(3) 03/98	3.11	25.0	**8:1**	2.91	21.0	**8:1**	3.50	23.5	**7:1**
(4) 05/98	3.40	26.2	**8:1**	3.11	21.2	**7:1**	3.39	29.6	**9:1**
(5) 06/98	3.73	26.8	**7:1**	3.79	26.6	**7:1**	5.09	24.5	**5:1**
(6) 08/98	3.38	26.4	**8:1**	3.75	16.3	**5:1**	3.09	21.4	**7:1**
(7) 10/99	3.10	24.8	**8:1**	2.70	26.4	**10:1**	2.90	22.9	**8:1**
(8) 01/00	3.39	25.7	**8:1**	2.39	21.9	**9:1**	3.10	24.0	**8:1**
(9) 03/00	3.50	26.0	**7:1**	3.10	25.0	**8:1**	2.80	27.0	**10:1**
Mean:	3.30	25.3		3.05	23.7		3.37	24.5	
SD ± s(r):	±0.38	±2.49		±0.51	±4.5		±0.69	±2.5	

Total rates:	% de N	% de C
Mean:	3.24	24.5
Interval:	2.39 – 5.09	16.3 – 32.3

% of OM* = 1.72.%C: total mean = 42.1%; interval of rates: 28.0% - 55.6% of OM

* By multiplying % of C by factor 1.72 the % of Organic Matter (OM) is obtained; (r) DP ±s – Standard Deviation; analyses are done in triple.

Table 7 also shows the ratio C:N, with intervals from 5:1 to 10:1. This means that, due to its nitrogen rate, sludge is good for agricultural use. Besides its good organic matter for the soil, its mineralization will not consume nutrient N in the environment and plants will not be impaired [21].

Concentrations of copper and other heavy metals in the biosolid are lower than maximum rates in the current Norms for the use of Sewage Sludge in Agriculture[57, 58, 59]. Consequently biosolids from STSs of Maringá may be used for agricultural purposes in so far as other conditions (restriction of place, soil capacity, recommended culture, maximum rate of application which depends on each element, and others) are observed.

CONCLUSIONS

From the experimental data above, we may conclude that:

a) there was no significant difference, at 5% level, in STSs' input sewage, with regard to copper;

b) in the case of copper and other heavy metals analyzed, RALF sewage system undertakes output without further need of any other treatment;

c) there was no significant difference, at 5% level, in sludge from the three STSs throughout the collection period;

d) total mean copper concentration in biosolid, 0.74 mg g^{-1}, is higher than the world average, although it is lower than the maximum limit, and thus proper for agricultural use;

e) there was no significant difference, at 5% level, in organic matter rate and in ratio C:N of sludge from the three STSs, and is thus recommended for agricultural use.

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DETERMINATION OF trans-RESVERATROL IN SOME ROMANIAN WINES AND SPIRITS

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ABSTRACT

Resveratrol, a phytoalexin of the hydroxystilbene group, is widely beneficial to health. It has been shown to posses anti-oxidative, anti-carcinogenic, anti-tumor and anti-viral properties. The concentration of trans-resveratrol in some Romanian wines and spirits has been measured using a direct injection isocratic UV-HPLC (Ultra Violet – High Liquid Pressure Chromatography) method. The experimental values obtained ranged from 0,10 mg/L for Cognac Murfatlar to 2,32 mg/L for Cabernet Sauvignon from the Dealu Mare Region.

KEYWORDS: trans-resveratrol, Romanian wines

RESUMO

Resveratrol, uma fitoalexina do grupo do hidroxiestilbeno , é altamente benéfico para a saúde. Foi demonstrado que o resveratrol possui propriedades anti-oxidativas, anti-carcinogênicas, anti-tumorais e anti-virais. A concentração de trans-resveratrol foi determinada em alguns vinhos e cognacs da Romênia usando método de injeção isocrática direta e Cromatografia Líquida de Alta Pressão (CLAP). Os valores experimentais obtidos, variaram de 0,10 mg/L para Cognac Murfatlar até 2,32 mg/L para Cabernet Sauvignon da Região de Dealu Mare.

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INTRODUCTION

Resveratrol, a phytoalexin of the trans-stilbene group, is found in grapes, peanuts, berries, pines, many medicinal and non-medicinal plants and in red wines.

The beneficial effects of wines , in particular red wines, have been known since ancient times and are probably due to a combination of the large number and variety of chemical compounds present in grapes and wine , including amino acids, hydrocarbons, alcohols, aldehydes, esters, sugars, glucosides, organic acids, phenols, polyphenols , vitamins, enzymes, tannins, anthocyanins, flavins, flavans, inorganic salts, etc. [1-5]

Recently, resveratrol has been pointed out as the component of wine more beneficial to health, has been used to explain the so-called "French paradox" and has been shown to posses anti-oxidative, anti-tumor , anti-carcinogenic and anti-viral properties.

The compound of particular interest is trans-resvertatrol (trans-3,4',5-trihydroxystilbene), whose structure is illustrated in Figure l. As can be seen, it can be considered a precursor of diethytlstilbestrol, estradiol and other hormones.

Aryl derivatives of trans-stilbene have been shown to be good liquid scintillators, in addition to having physiological properties. [6,7]

In a simple-minded approach, trans-resveratrol has been recently begun to be considered a miraculous compound, "The Chateau Hormone", responsible for good health, longevity, a cure-all panacea and a possible explanation of the "French paradox", very much alike the elixir of long life or the philosopher's stone of Alchemy.

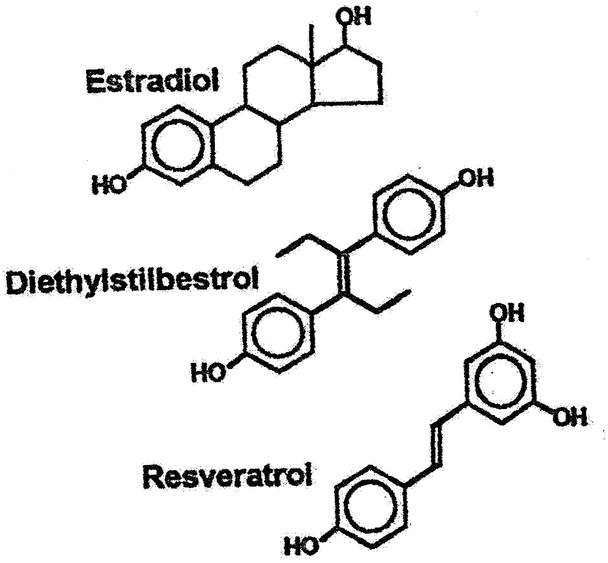

Figure 1. Structure of trans-resveratrol and related compounds

The population of many countries of Southern Europe, including France, Italy, Spain, Portugal, Croatia, Greece, Albania, Bulgaria and Romania suffers little heart disease, in spite of a diet that is relatively rich in fat. This fact has been explained by the regular consumption of red wine in moderate amounts and has been called the "French paradox". [9-12]

S. Renaud and M. De Lorgeril[9] studied the relationship between wine, alcohol, platelet function and coronary heart disease, while D. M. Goldberg and coworkers[10] suggested the apparent ability of moderate consumption of red wine to reduce the risk of cardiovascular disease.

B. D. Gehm, J. M. McAndrews P.Y. Chien and J. L. Jameson[11] showed that resveratrol found in grapes and wine is an agonist for the estrogen receptor, concluded that resveratrol is a phytoestrogen, that its estrogenic actions broaden the spectrum of its biological actions and that it may be relevant to the reported cardiovascular benefits of drinking red wine.

On the other hand, P. Kopp[12] , after analyzing a variety of studies done with resveratrol, concluded that whether resveratrol is indeed implicated in the explanation of the "French paradox" remains to be shown. According to him, currently there is no information on the serum concentration of resveratrol after

red wine consumption, nor its exact fate after ingestion and we can only speculate how much and which vintage of "Châteu Hormone" we should drink in order to benefit from the effect of resveratrol, while avoiding the potentially detrimental actions of ethanol.

More recent studies by M. Buluk and E. Demirel-Yilmaz[13] have shown that resveratrol decreases calcium sensitivity of vascular smooth muscle, enhances cytosolic calcium increase in the endothelium and causes independent relaxation of the vascular smooth muscle.

The chemopreventive activity of resveratrol in several types of cancer and the protective effects of polyphenols in oxidative stress have also been reported. M. Alkhalf and A. M. El-Mowafy have demonstrated that resveratrol activates adenylyl cyclase in human breast cancer cells and that it also has a potent antiproliferative effect on human osteosarcoma. [14]

R. Rodrigo and G. Rivera have studied in detail the protective effects of red wine in renal damage mediated by oxidative stress. [15]

EXPERIMENTAL PROCEDURE

The experimental procedure used was essentially described by A. A. Souto and coworkers.[16] The HLPC system employed was composed of a Perkin – Elmer 785A UV-Vis detector adapted for stopped-flow scanning (190-360 nm), a PE Series 200 pump, a PE 900 Series Interface and a PE Series 200 vacuum degasser. An octadecyl column 250 mm long was used, with 5µm particle diameter and 4.5mm inside diameter (Brownlee, Norwalk, USA). After filtration using a 0.45mm membrane, the samples were diluted six times with eluent and directly injected through a 20 µL loop into a C18 guard column. Reversed phase HPLC was performed with an isocratic elution (1.5 mL/min) using a solution of water-acetonitrile (75:25) as the eluent. The signal was monitored at 306 nm . The trans-resveratrol standards were supplied by Pharma Science, Inc., Montreal, Quebec, Canada. The wines and spirits analyzed were obtained from commercial suppliers in Romania. For quantification, an external standard calibration curve was done ranging from 0.10 to 10.0 mg/L of trans-resveratrol. The square

regression coefficient of the analytical curne was near unity (r2 = 0.9986) Data were processed by Turbo Chrom 4.0 software.

RESULTS AND DISCUSSION

A representative HPLC chromatogram is illustrated in Figure 2.

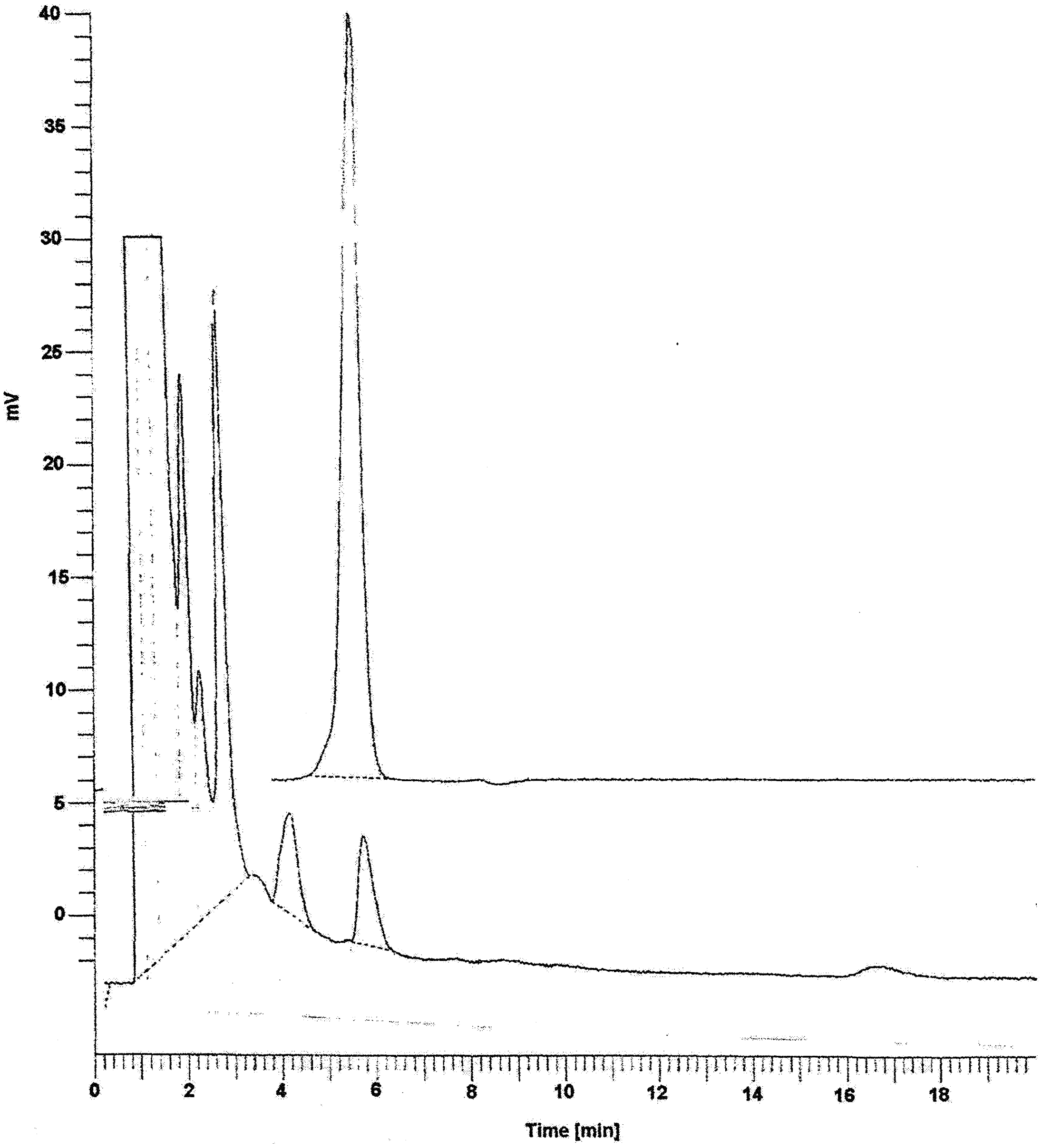

Figure 2. Typical HPLC chromatogram of a trans-resveratrol standard solution (top) and a diluted wine sample of Cabernet Sauvignon from Dealu Mare.

Some typical results obtained for the chromatographic analyses for the different Romanian wines and spirits are shown in Table I.

Table I. Concentration of trans-Resveratrol in Some Romanian Wines and Spirits.

Wine	Year	Conc. mg/L
Cabernet Sauvignon (Dealu Mare)	1984 1991	2.32 2.02
Cabernet Sauvignon (Murfatlar)	1997 1998	1.38 1.42
Dacia-Feteasca Albã (Cotnari)	1998 1993 1999	0.52 0.40 0.33
Pinot Gris (Murfatlar)	1992 1999	0.10 0.09
Muscat Otonel (Murfatlar)	1997	0.14
Sampanie –Silvania-Sec (Salaj-Zalau)	1991	0.12
Cognac (Murfatlar)	1998 1999	0.12 0.14
Apricot Brandy (Murfatlar)	1997	0.10
Palinca (Alba Iulia)	1992	0.11
Cognac Fortuna (Focsani)	1995	0.05
Rachiu (Alibunar-Banat-Yugoslavia)	1992	0.14

The concentration of trans-resveratrol determined in Romanian white wines and spirits varied from 0.10 to 0.52 mg/L. These values were expected and are typical of white wines that are known to contain lesser amounts of resveratrol. The highest value measured for a white wine was for Feteasca Alba from the Cotnari Region.

The cognacs and brandies analyzed showed small amounts of resveratrol (~0.10 mg/L), as expected.

The red wines presented values that ranged from 1.38 to 2.32 mg/L. The highest value was observed for Cabernet Sauvignon from Dealu Mare (1984 Vintage). The value of 2.32 mg/L can be considered significant, when compared to

other red wines from around the world (0.20 -5.06 mg/L) and taking into account the age of the wine.

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ANILDO BRISTOTI, A PIONEER IN SCIENCE IN RIO GRANDE DO SUL, BRAZIL

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ABSTRACT

Anildo Bristoti was born in São Francisco de Paula, Rio Grande do Sul, Brazil in 1936 and passed away in 2004. He studied chemistry, physics and mathematics and obtained a Doctor of Engineering Degree from UCLA in 1970. His main research interests were renewable energy sources and he was instrumental in the establishment of graduate programs in science and engineering at various universities in Southern Brazil. He trained more than one hundred research scientists presently working in chemistry, physics, engineering and materials science.

KEY WORDS: History of science and engineering, science in Brazil

RESUMO

Anildo Bristoti nasceu em São Francisco de Paula, Rio Grande do Sul, Brasil em 1936 e faleceu em 2004. Estudou química, física e matemática e obteve o grau de Doutor em Engenharia da Universidade da California em Los Angeles (UCLA) em 1970. A sua área principal de pesquisa tratava de fontes renováveis de energia e ele foi responsável pelo establecimento de programas de pós-graduação em ciência e engenharia em várias universidades no sul do Brasil. Ele preparou mais de cem pesquisadores, atualmente desempenhando atividades em química, física, engenharia e ciência dos materiais.

PALAVRAS CHAVE: história da ciência e da engenharia, ciência no Brasil

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Anildo Bristoti was born on March 28, 1936 in São Francisco de Paula, Rio Grande do Sul (RS) , Brazil and passed away in an automobile accident near Três Coroas, RS, on April 24, 2004.

He studied chemistry, physics and mathematics at the Pontificial Catholic University of Rio Grande do Sul (PUCRS) , Porto Alegre, and graduated in mathematics from the Federal University of Rio Grande do Sul (UFRGS) in 1960.

He was awarded the Master of Science Degree in Physics from the University of California at Los Angeles (UCLA) in 1967 and the Doctor of Science Degree in Energy Engineering from the same institution in 1970.

Dr. Anildo Bristoti held various administrative positions. Among them, we mention those of Chairman of the Physics Department of the Federal University of Rio Grande do Sul (UGRGS), Director of the Graduate Program in Metallurgical and Materials Science Engineering (UFRGS), Coordinator of the Nucleus of Energy (UFRGS), Secretary of the State Commission on Energy (CENERGS), Scientific Advisor of the Graduate School of the Pontificial Catholic Unbiversity of Rio Grande do Sul (PUCRS) and Director of the Graduate Program in Engineering (Energy, Environment and Materials) at the Lutheran University of Brazil (ULBRA) in Canoas, RS.

He gave classes at various universities at the undergraduate and graduate levels in physics, materials science, chemistry and engineering.

His main research interests dealt with renewable energy sources, energy use and energy planning, but he also worked in urban and regional planning, organic chemistry, thermodynamics, chemical and electrical engineering.

Prof. Dr. Anildo Bristoti served as research advisor of approximately sixty (60) graduate students for the Master or Doctor Degrees mainly at UFRGS and during the later years at ULBRA. Most of his former students and collaborators are presently working in engineering, physics or chemistry in Brazil or the southern part of continent. A representative list of some of his publications is to be found at the end of this article.

We first met Prof. Dr. Anildo Bristoti soon after our arrival in Porto Alegre in 1983. At the time, he was Director of the Master Degree Program in Metallurgical and Materials Science Engineering (PPGEM) at UFRGS and he invited us to participate as Professor and Research Advisor. Since then, we worked together first in the PPGEM Program, afterwards in the Department of Physical Chemistry at UFRGS, at PUCRS and during the last years at the Lutheran University of Brazil (ULBRA) in Canoas.

At the School of Engineering of the Federal University of Rio Grande do Sul (UFRGS), Anildo Brestoti was instrumental in establishing the Doctoral Program in Metallurgical and Materials Science Engineering (PPGEMM) together with ourself (LGI), Adão Mautone, Ildon Brochardt, Lourdes Iduwirges Müller, Lírio Schaeffer and Arno Müller and also played an important role in the Graduate Programs in Electrical Mechanical and Civil Engineering.

In the Chemistry Institute of the same university, Prof. Dr. Anildo Bristoti, together with Prof. Dr. José Schifino and our person was a member of the Founding Commission (1965) and the first Coordinating Commission of the Graduate Program in Chemistry (CPGQ). In addition, he was a champion of morality and fought widespread corruption and embezzlement of public funds within the Instituto de Química of the Federal University of Rio Grande do Sul (UFRGS).

Anildo Bristoti was the first scientist to use extraction with supercritical fluids in Rio Grande do Sul and the only person that we know in Brazil to teach and advanced course in irreversible thermodynamics.

PROF. DR. ANILDO BRISTOTI (1936-2004)

From 1997 to 2004, he participated mainly in various graduate programs at the Lutheran University of Brazil (ULBRA) in Canoas. Among them, we mention the Graduate Program in Science, and the Graduate Program in Engineering, Energy, Environment and Materials. He died near Três Coroas and Igrejinha, on a Saturday morning , on his way to ULBRA in Canoas, where he was going to teach a class , part of the Graduate Program in Engineering (PPGEAM).

He was a member of the Editorial Board of the *Brazilian Journal of Materials Science and Engineering* and of *Technología,*

Partial view of the Ecological Park (Parque das Cachoeiras – Park of the Waterfalls) near São Francisco de Paula established by Dr. Anildo Bristoti,

The major preoccupation during his entire life was was the divulgation of scientific knowledge, not only among the more educated, but also among the common people. He participated in and supervised in many extension programs and gave lectures throughout the whole state. Anildo Bristoti was a descendant of Italian immigrants that settled in the mountain region of Rio Grande do Sul. He often used to say that it was by a strike of luck that he obtained a higher education.

A few years before his death, he opted for the Italian citizenship and in homage to his ancestors changed his name from Bristoti to the original Bristot.

The guidelines of his life were renewable energy sources, sustainable development and preservation of nature. He helped establish and build many alcohol microdistilleries using sugar cane as raw material and was responsible for many projects involving generation and distribution of electricity. Prof. Dr. Anildo Bristoti spent his life savings to purchase and establish the *Parque das Cachoeiras – Park of the Waterfalls*, an ecological reserve area near his native town of São Francisco de Paula.

Those of us who had the privilege to know and collaborate with Prof. Dr. Anildo Bristoti will remember him as a good person, morally correct, always ready to help, full of enthusiasm and positive thinking.

Anildo Bristoti was a pioneer in science and a dreamer. For him everything was possible. The precarious, primitive and poor laboratory conditions were no impediment to do research. He was a good an efficient leader, a first class motivator and a specialist in group dynamics. He definitely left his marks on the development of science and engineering in the State of Rio Grande do Sul.

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CATARINA, SOUTH AMERICA` S FIRST HURRICANE. A SIGNAL OF GLOBAL CLIMATIC CHANGES

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ABSTRACT

On March 27, 2004 a strong storm (tropical cyclone) hit the coast of Southern Brazil and caused death and widespread devastation in part of the States of Santa Catarina and Rio Grande do Sul. In spite of what some Brazilian meteorologists initially had to say, Catarina was South America's first hurricane. Many Brazilian meteorologists, for various reasons, did not want to recognize that it was a real hurricane and classified the phenomenon as an extratropical cyclone, a polar low or even a hybrid occurrence. Catarina initiated about 1000km off the Brazilian Coast (Santa Catarina) around March 20, 2004 as an extratropical cyclone (EC), underwent tropical transition (TT) and subsequently became a cathegory I hurricane. It was really South America's first hurricane and it may be a possible indication of global climate changes.

RESUMO

Em 27 de Março de 2004 uma grande tempestade (ciclone extratropical) atingiu o Sul do Brasil, incluindo parte dos Estados de Santa Catarina e Rio Grande do Sul. A maioria dos meteorologistas brasileiros, por várias razões, não quis reconhecer que de fato se tratava de um verdadeiro furacão e classificou o acontecimento como um ciclone extratropical (CE), um fenômeno híbrido ou algo similar. Catarina começou á cerca de 1000km da costa do Brasil (Santa Catarina) em torno de 20 de Março de 2004 como um ciclone extratropical (CE), foi sujeito á um transição tropical (TT) e subsequentemente se transformou num furracão de categoria I. Foi verdadeiramente o primeiro furacão observado na América do Sul e pode ser uma possível indicação de mudança climática global.

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A *hurricane* is an intense storm of tropical origin with wind speeds exceeding 120 km/hr (64 knots or 74mi/hr) which forms over warm waters of the Northern Atlantic and Eastern North Pacific Oceans. The word hurricane comes from the Mayan storm god, *Hunraken*. In general, a hurricane is a large rotating storm where the winds move around a relatively calm center called the eye. In the Western Pacific the hurricanes are called *typhoons*, in the Philippines *baguios* and *cyclones* in India and Australia.

Hurricanes arise from tropical cyclones that spiral off the west coast of Africa and Central America, usually in the later summer and early fall. They lash the Caribbean, the Atlantic Coast States of the U.S. and at times they also hit Mexico from the Pacific. Typhoons arise from tropical cyclones, reach the coast along the Northwest Pacific Ocean and usually hit Japan, Korea and the Philippines. Cyclones (that are really typhoons or hurricanes) also hit at times India, Australia, Tahiti, Fiji and Samoa. Arctic cyclones (winter storms) that pack hurricane force winds are formed at times in the North Atlantic and may batter the British Isles. Figure 1 illustrates the regions where hurricanes usually form and the pathways they usually take.[1-3]

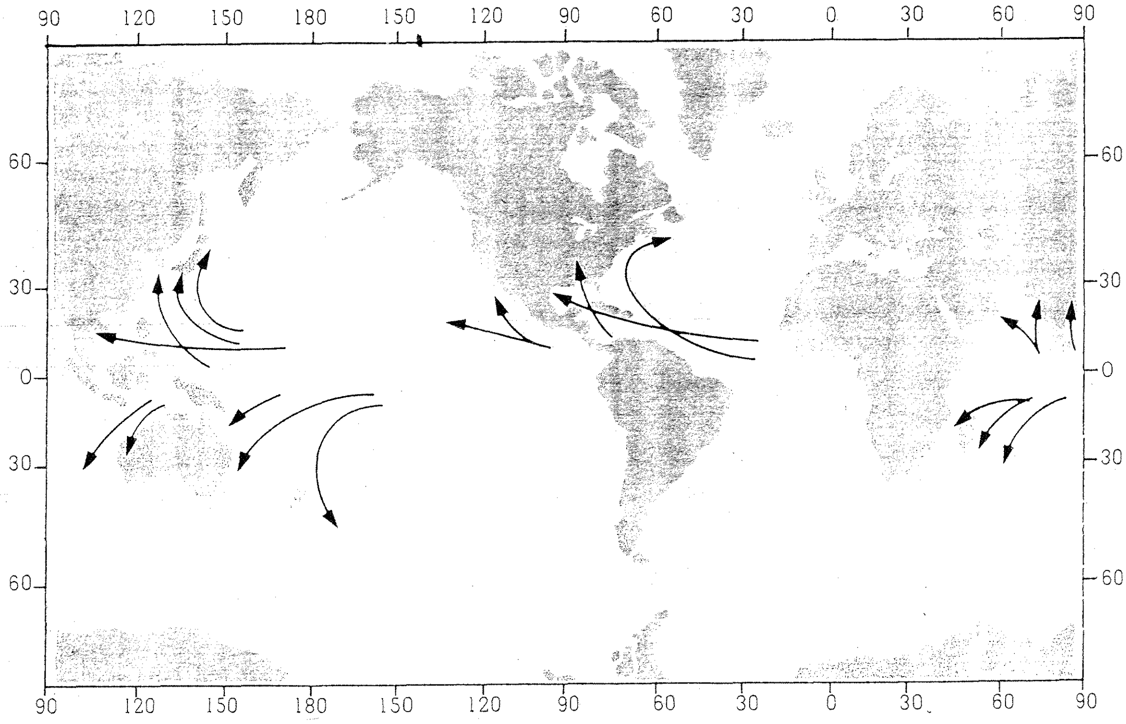

Figure 1. Regions of the Earth where hurricanes usually form and the pathways they commonly take.

Strangely, South America is generally believed to be protected from hurricanes. They do not form off the west coast because the water of the Pacific is too cold and strong winds over the South Atlantic shear off the tops of developing cyclones before they reach peak power.[4-11]

Hurricane form over tropical waters where the winds are light and the surface water temperature is warm over a vast area. Sea surface temperature is usually above 26.5 °C and at a depth of 50m. This type of conditions prevail over the tropical North Atlantic and North Pacific Oceans during the summer and early fall. Normally, the hurricane season lasts from June to November.

In order for a mass of unorganized thunderstorms to develop into a hurricane, the surface winds must converge. In the Northern Hemisphere, converging air spins counterclockwise, while in the Southern Hemisphere the spinning is clockwise. This type of rotation does not develop on the equator where the Coriolis force is zero. A distance of about 10° latitude from the equator is necessary for a Coriolis Effect strong enough to prevent filling of the central low pressure (center of the hurricane).

Hurricanes form in subtropical regions, usually between 10° and 20° latitude.

Convergence may occur along a front that has moved from middle latitude into the tropics. Developing thunderstorms and converging surface winds may form, particularly when the front is accompanied by a cold upper level trough. Surface winds converge along the intertropical convergence zone (ITCZ). Sometimes, when the ICTZ is displaced away from the equator, a wave in the ITCZ forms into an area of low pressure, convection becomes organized and the system grows into a hurricane.[1-3]

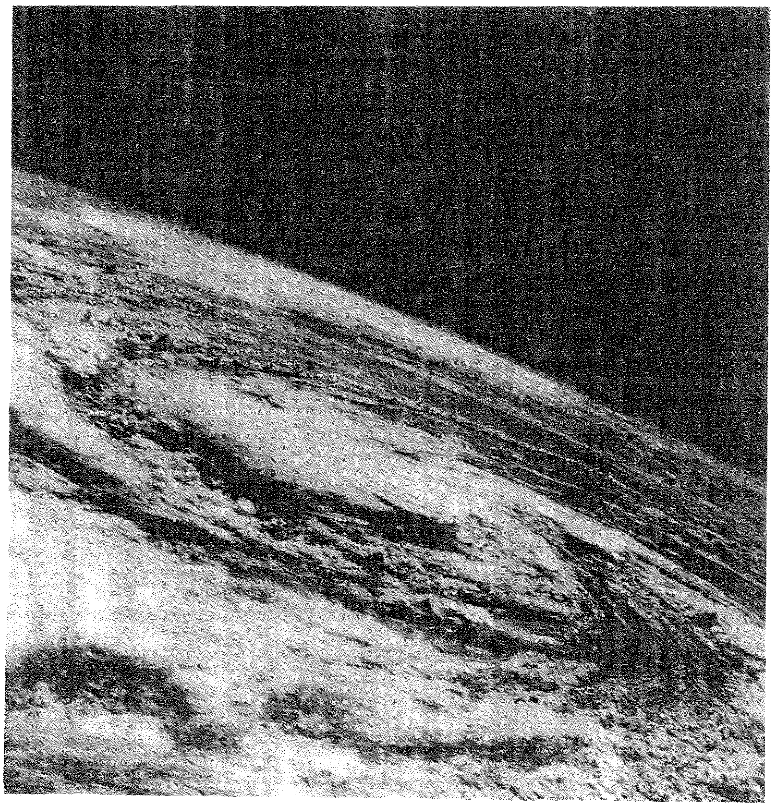

Figure 2.Photograph from the Apollo 7 spacecraft of hurricane Gladys about 150km southwest of Tampa, Florida (Courtesy of NASA –National Aeronautics and Space Administration and Sarmisegetusa Research Group-SRG, Santa , New Mexico, USA)

Figure 2 shows Hurricane Gladys, a typical hurricane. The picture was taken from the Apollo 7 Spacecraft when the storm was off the coast of Florida. A typical hurricane has a diameter of approximately 500km. The area in the center is called the eye and its diameter usually varies from 20 to 50km. Within the eye, the winds are light and clouds are usually broken. The surface air pressure is very low, usually about 950mb. The dark blotches in the eye correspond to regions where the sky is clear. The clouds align themselves in bands (*rain bands*) that spiral in towards the storm center where they wrap themselves around the eye. The surface winds increase in speed as they blow counterclockwise (Northern Hemisphere) and inward toward the center. Around the eye is the eye wall, a ring composed of intense thunderstorms that whirl around the storm center and may extend upward to about 15km above the sea level. The strongest winds and the heaviest precipitation are normally found within the eye wall. At times the winds may surpass 120 knots.

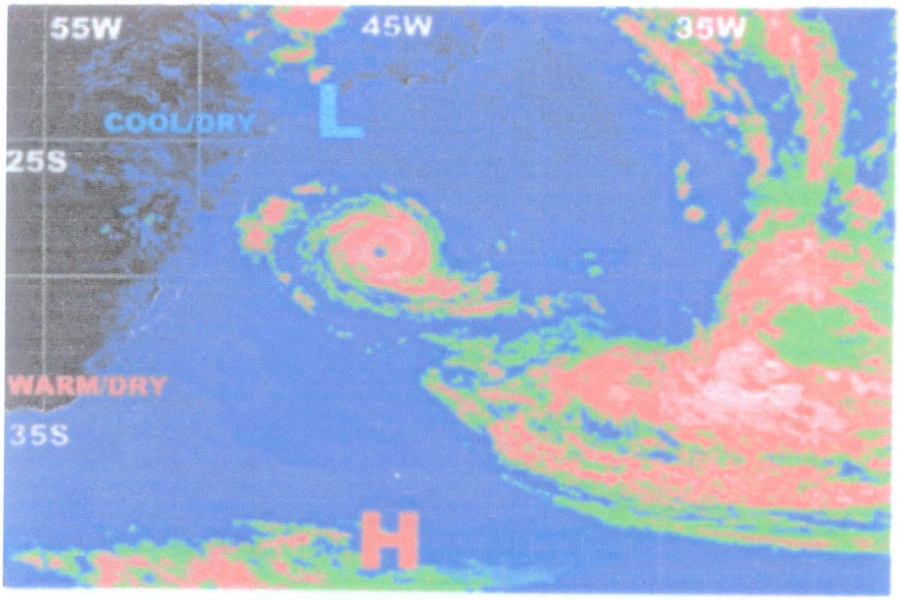

Figure 3. Enhanced image of Catarina obtained from the GOES-12 infrared channel. (Courtesy of NASA and Sarmisegetusa Research Group, Santa Fe, New Mexico, USA)

Figure 3 is an enhanced image from the GOES -12 meteorological satellite infrared channel obtained on March 26, 2004 showing Catarina approaching the Brazilian Coast. The position of the upper level ridge and trough is indicated by letters H and L, respectively. Regions of warm/dry and cool/dry surface air over the continent are also shown.

Figure 4 is a three–dimensional image of Catarina on May 27 2004 obtained from the National Aeronautics and Space Administration –NASA. The hurricane had a diameter of about 400km and the eye had a diameter between 25 and 40km. The estimated minimal central pressure inside the eye was estimated about 974 hPa or mb.

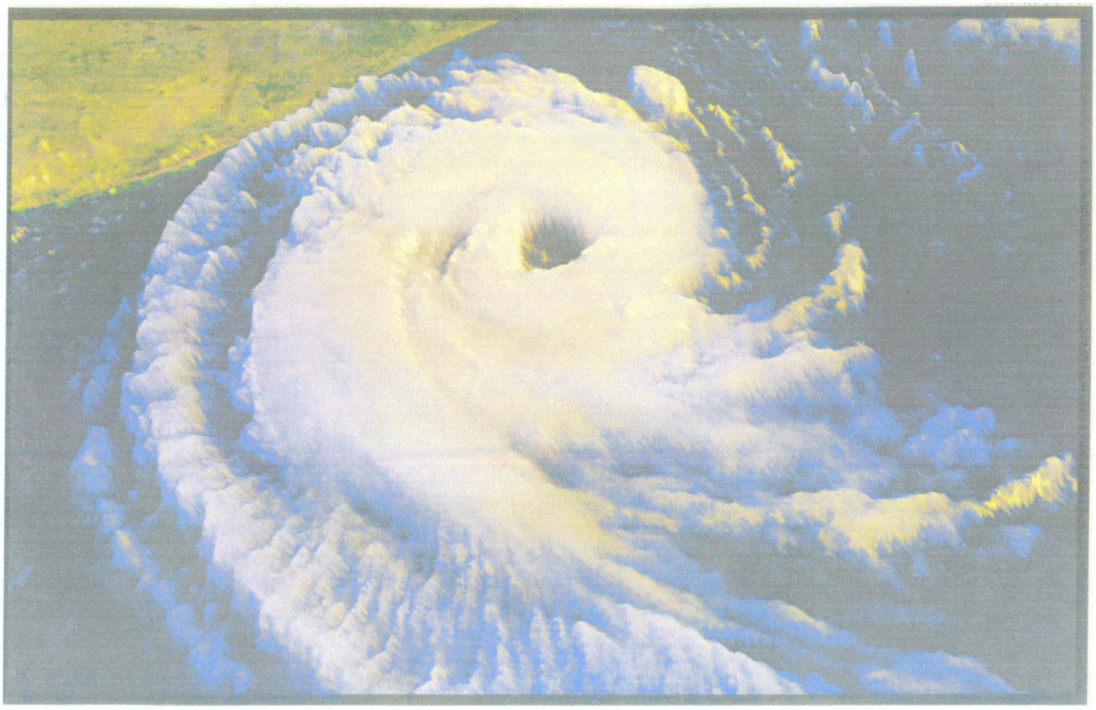

Figure 4. Three-dimensional image of Catarina on March 27, 2004 obtained from NASA (Courtesy NASA and Sarmisegetusa Research Group, Santa Fe, New Mexico, USA).

The surface winds had hurricane force and ranged between 120 and 150km/hr. According to the criteria described above, Catarina was classified as a type I hurricane on the Saffir-Simpson scale. During its trajectory, Catarina covered a route of more than 3000km.[4-12]

According to available meteorological data, Catarina began as an extratropical cyclone (EC) in a frontal system around March 20, 2004 about 1000km off the coast of the Brazilian State of Santa Catarina. Two days later it underwent tropical transition (TT) under continuous low vertical wind shear over average water temperatures. Subsequently, Catarina reached cathegory I hurricane strength under an unusual combination of low wind shear and strong mid to high latitude blocking.

Meteorologists like Jack Bevan of the National Hurricane Center of the United States in Miami, Florida, observed the hurricane three days before it hit the Brazilianm Coast and monitored its course and development. Brazilian authorities were informed unofficially about the unusual phenomenon.

On the other hand, Marcelo Seluchi, Director of CPTEC (Centro de Previsão do Tempo e Estudos Climáticos) of the Instituto Nacional de Pesquisas Espaciais-INPE in São José dos Campos, SP, and other Brazilian meteorologists insisted initially that Catarina was an extratropical cyclone (EC), that its center was colder than its rims and that the winds were spinning in the same direction at the surface and higher levels.[5]

Catarina is the first South Atlantic hurricane that has been documented to the present date. There are two other cases of weak tropical cyclones (TC) below hurricane strength that may have happened during the era of satellite monitoring.

Large scale phenomena and anomalies at mid to high latitudes may be related to the mechanism that led to the formation of this hurricane.[6-11] Catarina may be a signal of global climatic change.

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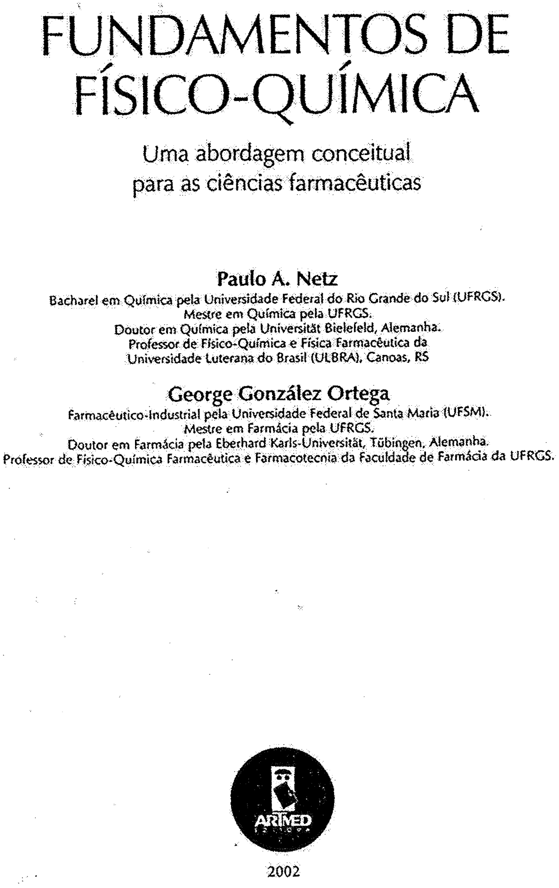
BOOKS /LIVROS

PAULO A. NETZ,GEORGE GONZÁLEZ, "*Fundamentos de Físico Química- Uma abordagem para as ciências farmacêuticas*" , Editora Artmed, Porto Alegre, RS, Brasil,2002, 299 p.

"*Fundamentos de Físico-Química*" é um livro introdutório para alunos do curso de Farmácia do Brasil. Como pode ser visto no Sumário, o livro texto fundamental aborda os principais aspectos da Físico-Química. O conteúdo, como um todo, é relativamente bem elaborado e contem muitos exemplos ilustrativos. Surge porém uma dificuldade em avaliar o rigor e o nível do texto como um todo.

FUNDAMENTOS DE
FÍSICO-QUÍMICA
Uma abordagem conceitual
para as ciências farmacêuticas
Paulo A. Netz
George González Ortega



FUNDAMENTOS DE
FÍSICO-QUÍMICA
Uma abordagem conceitual
para as ciências farmacêuticas

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Analisando o livro e lendo o Prefácio, aqui reproduzido *ad integra* não ficou muito clara a intenção dos autores nem quanto ao rigor matemático necessário para os alunos de farmácia entender Físico-Química nem como vai ser possível para ao futuros farmacêuticos entender " as relações entre as grandezas físico-químicas e aplicar qantitativamente esse conhecimento à situações concretas".

Prefácio

A atividade do famacêutico, por ser essencialmente aplicada, pressupõe um razoável conhecimento de uma gama deaspectos de várias ciências básicas correlacionadas, tais como química, física e biologia. Somente a compreensão dos fenômenos subjacentes à técnica e à ação famacêuticas permitem-lhe ir além do conhecimento empírico.

A relação entre o conhecimento farmacêutico e essas ciências é, contudo, uma relação que vai além do fornecimento de uma mera base necessária para a compreensão isolada desse conhecimento. Mais do que isso, tal relação deve permitir a construção de elementos capazes de racionalizar, de maneira lógica e sistemática, os saberes empíricos e dotá-los de uma visão de conjunto, inserindo-os em um todo. Com a gigantesca expansão do saber científico e técnico, a possibilidade de uma compreensão do todo, de uma racionalização, é necessária para a sua apropriação e utilização produtiva e criativa. Não basta saber e saber aplicar: quando se quer ir além, é necessário saber o que está "por trás".

O estudo da físico-química em um curso de Farmácia insere-se neste espírito. A físico-química fornece uma base conceitual para as diferentes áreas dentro da química, da tecnologia e da biologia ao analisar, sistemática e quantitativamente, conceitos centrais como energia, equilíbrio, transformações, espontaneidade e velocidade de reações. A físico-química contribui, assim, para encadeamentos relevantes para o farmacêutico, bem como para fornecer subsídios necessários para muitos dos procedimentos técnicos do dia-a-dia profissional.

Devido à sua estrutura em grande parte axiomática, baseada em poucos conceitos centrais e suas inter-relações, a físico-química apresenta um caráter eminentemente matemático; é essencialmente uma ciência com poucos pressupostos genéricos aplicados a contextos bem-específicos, e a matemática auxilia o caminho desde a base até a aplicação. Somente por intermédio da matemática é possível entender as relações entre as grandezas físico-químicas e aplicar quantitativamente esse conhecimento às situações concretas. Longe de se constituir em um empecilho, a vocação matemática da físico-química deve servir para mostrar a elegância e a concisão – isto para não falar na "economia de informações" – de uma abordagem abstrata.

O preparo matemático, todavia, costuma ser bastante díspar nos diferentes cursos de Farmácia. Na maioria das vezes, nota-se uma ausência no currículo do cálculo diferencial e integral, lacuna que se constitui em uma dificuldade adicional – de fato, uma grande dificuldade – para a compreensão da físico-química, pois o cálculo é uma ferramenta necessária tanto à dedução das fórmulas quanto à aplicação e à contextualização dos princípios e dos conceitos da termodinâmica em diversas situações particulares.

Em decorrência dessa situação, os livros usuais de físico-química, principalmente os disponíveis em língua portuguesa, acabam não sendo bem-recebidos pelos farmacêuticos. Por um lado, porque essas obras dedicam-se prioritariamente a um público de químicos e de engenheiros químicos; por outro, porque o seu nível matemático baseia-se no cálculo diferencial e integral e acaba afastando o público matematicamente menos preparado. A literatura disponível em físico-química em inglês ou em espanhol acaba se enquadrando nos mesmos problemas, ou, eventualmente, embora direcionada de fato para as ciências farmacêuticas, exibe um nível de detalhe e uma exigência de conhecimentos prévios por vezes muito elevados.

Para suprir essa lacuna, procuramos desenvolver um livro em língua portuguesa que tratasse dos fundamentos de físico-química de um ponto de vista suficientemente simples, matematicamente falando, porém profundo o suficiente para fornecer a base necessária para temas de elevada relevância profissional. Uma obra que procurasse delinear toda a base do conhecimento de físico-química adequada para um curso de graduação, escolhendo, porém, exemplos prioritariamente oriundos do cotidiano farmacêutico para ilustrar os conceitos, as equações e as definições. Um trabalho desse tipo deve, necessariamente, dar uma grande ênfase à discussão conceitual, à compreensão do que está por trás das fórmulas e das equações. Trata-se de primeiro entender o conceito daquilo que se fala e, depois, entender como se descreve tal conceito. Esse foi o objetivo que tivemos em mente ao elaborar esta obra e esperamos que tenha sido alcançado.

Logo após a discussão dos conceitos no *texto principal*, no qual o preparo matemático exigido é apenas elementar, segue a aplicação dos conceitos estudados em *exemplos*, estruturados como exercícios resolvidos. Apesar de priorizar a abordagem conceitual – a descrição –, nosso texto busca, também, satisfazer à necessidade daqueles que procuram um maior rigor na exposição da matéria. Assim, reservamos um espaço em cada capítulo para o tratamento matematicamente rigoroso dos conceitos abordados. Estas seções, intituladas "Em detalhe", podem ser simplesmente ignoradas pelo leitor que não tiver interesse nelas. O seu estudo, porém, pode ser bastante compensador, pois, quando bem-entendida, a estrutura matemática da físico-química facilita o seu uso e torna desnecessário o tedioso trabalho de memorização interminável de fórmulas, fatos e conceitos. Isso requer, entretanto, um esforço consciente por parte do aluno, que deve estar disposto a buscar a sua própria superação por meio dos exercícios, da discussão dos pontos pouco claros, da contínua indagação, pois, somente assim, pode-se construir um conhecimento sólido, flexível e eficaz.

Bom proveito!

PAULO A. NETZ
GEORGE GONZÁLEZ ORTEGA

As seções intituladas “Em detalhe” podem ser de verdade “simplesmente ignoradas pelo leitor que não tiver interesse nelas “ com afirmam os autores?

Na nossa modesta opinião, a separação do tratamento matematicamente rigoroso em seções intituladas **“EM DETALHE”** parece tirar boa parte da linguagem matemática e deixar somente a descrição em português para elucidar conceitos no texto principal.

É muito difícil entender esta divisão por parte de dois profissionais formados como Doutores em Físico–Química na Alemanha, um na Universidade de Bielfeld e o outro na Universidade de Tübingen. A final, a Alemanha é a pátria de origem de Ostwald e tantos outros físico-químicos famosos e conceituados. Os farmacêuticos preparados desta maneira em Físico-Química dificilmemte irão além do conhecimento empírico e seguirão perpetuando o “Complexo Periférico” no mundo em desenvolvimento.

Aparentemente, os autores não conhecem livros clássicos com “*Basic Physical Chemistry for the Life Sciences*” de V.R., Williams e H. B. Williams e “*Introductory Physical Chemistry*” de D. H. Andrews e não mencionam o livro de G.M. Barrow traduzido em Espanhol faz muitos anos.

Como físico-químico que ministrou disciplinas para alunos das ciências da saúde por mais de quarenta anos em várias universidades nos Estados Unidos e no Brasil e participou do estabelecimento e/ou reestruturação de cinco Cursos de Farmácia no nosso País, sentimos a obrigação dar a nossa modesta opinião.

Lavinel G. Ionescu, A.A., B.S.,M.S., Ph.D.(Físico-Química)

PAULO A. NETZ, GEORGE GONZÁLEZ, “*Fundamentos de FísicoQuímica – Uma abordagem para as ciências farmacêuticas*”, Editora Artmed, Porto Alegre, RS, Brasil, 2002, 299p.

This book is an introductory physical chemistry text in Portuguese intended for pharmacy students in Brazil. The book is well planned and well written. There is however a major problem. Apparently the authors, in spite of what they state in the *Preface*, seem to think that it is possible to teach Physical Chemistry without the rigor Mathematics and have included the mathematical treatment as “a detail”.

Unfortunately, this kind of approach can only increase even more the gap between the first world and the developing countries.

Lavinel G. Ionescu, A.A., B.S., M.S., Ph.D. (Physical Chemistry)

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