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THEODORO AUGUSTO RAMOS – A BRAZILIAN CONTRIBUTION TO THE MODEL OF THE ATOM*

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ABSTRACT

The present article discusses the contribution of Theodoro Augusto Ramos, A Brazilian mathematician, to the model of the atom. In a paper entitled "The Theory of Relativity and the Spectral Lines of Hydrogen", *presented to the Brazilian Academy of Sciences in November 1923, Theodoro Ramos analyzed the fine spectra of the hydrogen atom using the principles of the general theory of relativity. His results represent an improvement of the Bohr-Sommerfeld model.*

RESUMO

O presente artigo trata da contribuição de Theodoro Augusto Ramos, um matemático brasileiro, para o modelo atômico. Num trabalho com título "A Theoria de Relatividade e as Raias Espectraes do Hydrogênio", *apresentado perante a Academia Brasileira de Ciências em Novembro de 1923, Theodoro Ramos analizou o espectro fino do átomo de hidrogênio usando a teoria de relatividade geral.Os seus resultados representam uma melhoria do Modelo de Bohr-Sommerfeld.*

KEYWORDS. Hydrogen Atom, Atomic Models, Fine Spectra, Theory of Relativity.

Theodoro Augusto Ramos (1895-1935) was one of the most notable and productive Brazilian mathematicians of his time. He graduated in civil engineering in 1917 from the Escola Politécnica of Rio de Janeiro, one of the traditional engineering schools of Latin America, founded as a military institution in 1792, soon after the arrival of the Portuguese Court in Brazil.

- Paper presented in part at the XLIV Brazilian Congress of Chemistry (Associação Brasileira de Química - ABQ), Fortaleza, Ceará, Brazil, September 20-24, 2004.

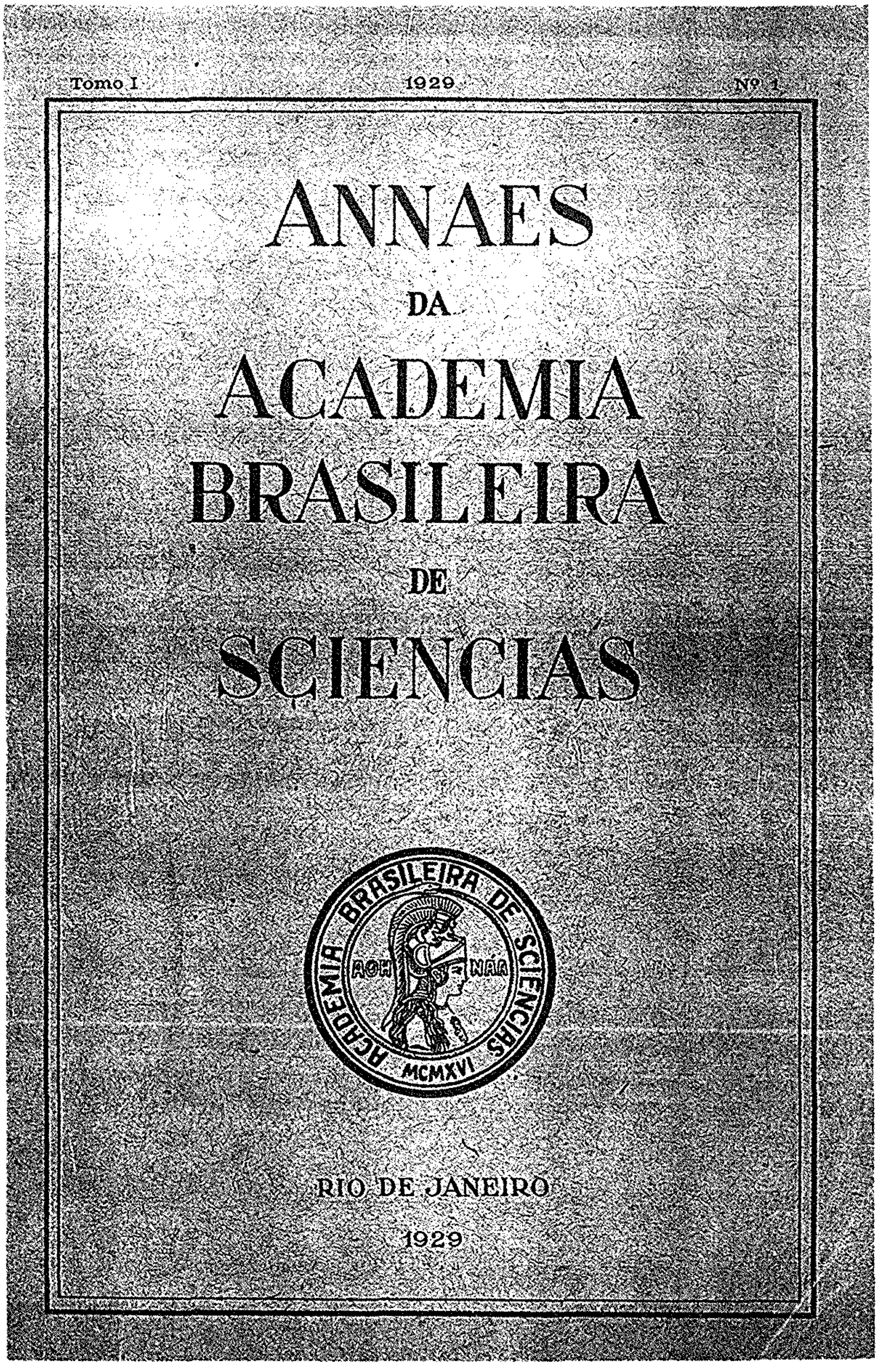
He obtained the Doctoral Degree in Physical and Mathematical Sciences from the same institution and his thesis was entitled "On Functions of Real Variables". During the same year he accepted a position in mathematics in the Engineering School (Escola Politécnica) of São Paulo. It was in São Paulo that Theodoro Ramos made his more important contributions to science and mathematics. He published various articles dealing with mathematical physics and several textbooks on advanced mathematics.

Theodoro Augusto Ramos (1895-1935)

He played an important role in the establishment of what is now the University of São Paulo and was a member of the Organizing Committee named by the Governor Armando Oliveira Salles. Theodoro Ramos was the first Dean of the Faculty of Philosophy, Sciences and Letters and was instrumental in inviting and bringing to Brazil during the early 1930's a large number of European scientists in mathematics, physics, chemistry and biology.

According to well-informed sources, Theodoro Ramos spent some time working with Niels Bohr in Copenhagen and was familiar with scientific circles in Europe.

The present paper deals with the contribution of Theodoro Augusto Ramos to the model of the atom. In November 1923, he presented a work entitled "*The Theory of Relativity and the Spectral Lines of Hydrogen*" to the Brazilian Academy of Sciences. The article was published six years later in the first issue of the *Annaes da Academia Brasileira de Sciencias* in 1929. Theodoro Ramos analyzed the fine spectra of the hydrogen atom using the principles of the general theory of relativity. Earlier, in 1923, Arnold Sommerfeld had explained the splitting of the Balmer lines of hydrogen analyzing the movement of the electron around the nucleus using the restricted theory of relativity.



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1929

A THEORIA DA RELATIVIDADE E AS RAIAS ESPECTRAES DO HYDROGENIO

THEODORO RAMOS

Sommerfeld conseguiu explicar o desdobramento das raias da série classica de Balmer relativa ao hydrogenio (1), estudando o movimento dos electrons em torno do nucleo positivo sob o ponto de vista da theoria da relatividade restricta (2). Sommerfeld suppoz um campo de Minkowski e desprezou o movimento do nucleo. G. Darwin (3), estudou a influencia deste deslocamento e achou um termo correctivo desprezivel para o afastamento das raias do "doublet".

Neste pequeno trabalho vamos abordar o problema sob o ponto de vista da theoria da relatividade generalizada.

O nucleo positivo será assimilado a uma esphera de raio a e de massa M e cuja carga electrostatica é E. Teremos um campo com symetria espherica em que são nullas as componentes do potencial vector.

O espaço-tempo no exterior da esphera será definido por (4)

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(1) Sommerfeld "La constitution de l'atome et les raies spectrales" t. 2, 1923.

(2) Mostramos em um trabalho anterior que o mesmo resultado póde ser obtido modificando ligeiramente o potencial electrostatico.

(3) C. G. Darwin, Phil. Mag. (1920), de accordo com a citação de Sommerfeld, op. cit., pg. 568, t. 2.

(4) Deve-se este ds^2 a H. Vanderlinden. Consulte-se a pg. 95 do excellente tratado de Th. De Donder "La Gravifique Einsteinienne". Este autor emprega um outro systema de constantes.

A THEORIA DA RELATIVIDADE E AS RAIAS ESPECTRAES DO HYDROGENIO

THEODORO RAMOS

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$$ds^2 = -\frac{dr^2}{1 - \frac{\gamma}{r} + \frac{\varepsilon^2}{r^2}} - r^2\left[d\theta^2 + sen^2\theta\, d\varphi^2\right] +$$

$$+ c^2\left(1 - \frac{\gamma}{r} + \frac{\varepsilon^2}{r^2}\right) dt^2$$

em que $\gamma = \frac{2fM}{c^2} + \frac{\varepsilon^2}{a}$ e $\varepsilon^2 = \frac{fE^2}{c^4}$,

f designando a constante de Gauss e c a velocidade da luz.

O movimento do electron de massa m e de carga e póde ser estudado no espaço e no tempo com o auxilio do principio generalizado da conservação da quantidade de movimento e da energia.

Ponhamos $L = mc^2\left[1 - V\right] + \frac{eE}{r}$

em que $V = \frac{1}{c}\,\frac{ds}{dt}$,

e consideremos o tensor $\omega_\delta = p_r\,\delta r + p_\varphi\,\delta_\varphi + p_\theta\,\delta\theta - W\,\delta t$,

cujas componentes de espaço são as quantidades de movimento generalizadas (1)

$$p_r = \frac{\delta L}{\delta r'}, \quad p_\varphi = \frac{\delta L}{\delta \varphi'}, \quad p_\theta = \frac{\delta L}{\delta \theta'}$$

(os accentos designando as derivadas em relação a t), e cuja componente de tempo é a energia total generalizada

$$W = r'\frac{\delta L}{\delta r'} + \varphi'\frac{\delta L}{\delta \varphi'} + \theta'\frac{\delta L}{\delta \theta'} - L$$

As equações differenciaes do movimento serão obtidas exprimindo que ellas admittem como invariante integral $\int_C \omega_\delta$ extendida a um contorno fechado qualquer no espaço a 7 dimensões $(r, \varphi, \theta, p_r, p_\varphi, p_\theta, t)$.

---

(1) Alguns autores dão a estas expressões a denominação de "momentos".

Obtem-se assim, mediante um calculo classico, as condições

$$dp_r + \frac{\delta W}{\delta r}\,dt = 0$$

$$-\,dr + \frac{\delta W}{\delta p_r}\,dt = 0$$

e mais 4 equações analogas para φ e θ, e tambem

$$-dW + \frac{\delta W}{\delta t}\,dt = 0$$

Como W não depende explicitamente de φ e de t, tira-se immediatamente $\frac{dp_\varphi}{dt} = 0$, $dW = 0$

$$p_\varphi = const. = p \qquad e \qquad W = const.\ ;$$

vem tambem $\frac{dp_\theta}{ds} = \frac{\delta W}{\delta \theta}\,\frac{dt}{ds}$

que desenvolvida dá

$$\frac{d}{ds}\left(r^2\,\frac{d\theta}{ds}\right) = r^2\, sen\,\theta\, cos\,\theta \left(\frac{d\varphi}{ds}\right)^2 .$$

Estas equações permittem concluir que a energia total generalizada é constante e que a trajectoria póde ser considerada como pertencente ao plano $\theta = \frac{\pi}{2}$.

As equações $p_\varphi = p$ e $W = const.$

dão, então, $mcr^2\,\frac{d\varphi}{ds} = p$

$$c\left[1 - \frac{\gamma}{r} + \frac{\varepsilon^2}{r^2}\right]\frac{dt}{ds} = \frac{W}{mc^2} + \frac{eE}{mc^2 r} + 1 .$$

Tem-se, tambem,

$$p_r = mc\,\frac{dr}{ds}\left[1 - \frac{\gamma}{r} + \frac{\varepsilon^2}{r^2}\right]^{-1}$$

$$c^2\left[1-\frac{\gamma}{r}+\frac{\varepsilon^2}{r^2}\right]\left(\frac{dt}{ds}\right)^2-\left[1-\frac{\gamma}{r}+\frac{\varepsilon^2}{r^2}\right]^{-1}\left(\frac{dr}{ds}\right)^2-$$

$$-r^2\left(\frac{d\varphi}{ds}\right)^2=1.$$

Eliminando $\frac{dt}{ds}$, $\frac{dr}{ds}$ e $\frac{d\varphi}{ds}$ entre estás 4 equações, vem

$$p_r^2=\left[\frac{W}{c}+\frac{eE}{r}+mc\right]^2\left[1-\frac{\gamma}{r}+\frac{\varepsilon^2}{r^2}\right]^{-2}-$$

$$-mc^2\left[1-\frac{\gamma}{r}+\frac{\varepsilon^2}{r^2}\right]^{-1}-\frac{p^2}{r^2}\left[1-\frac{\gamma}{r}+\frac{\varepsilon^2}{r^2}\right]^{-1}$$

Desenvolvendo em série

$\left[1-\frac{\gamma}{r}+\frac{\varepsilon^2}{r^2}\right]^{-1}$ e $\left[1-\frac{\gamma}{r}+\frac{\varepsilon^2}{r^2}\right]^{-2}$ conservando sómente os primeiros termos do desenvolvimento (o que é permittido pois $\frac{\gamma}{r}$ e $\frac{\varepsilon^2}{r^2}$ são muito pequenos) vem pará p^2_r a expressão approximada

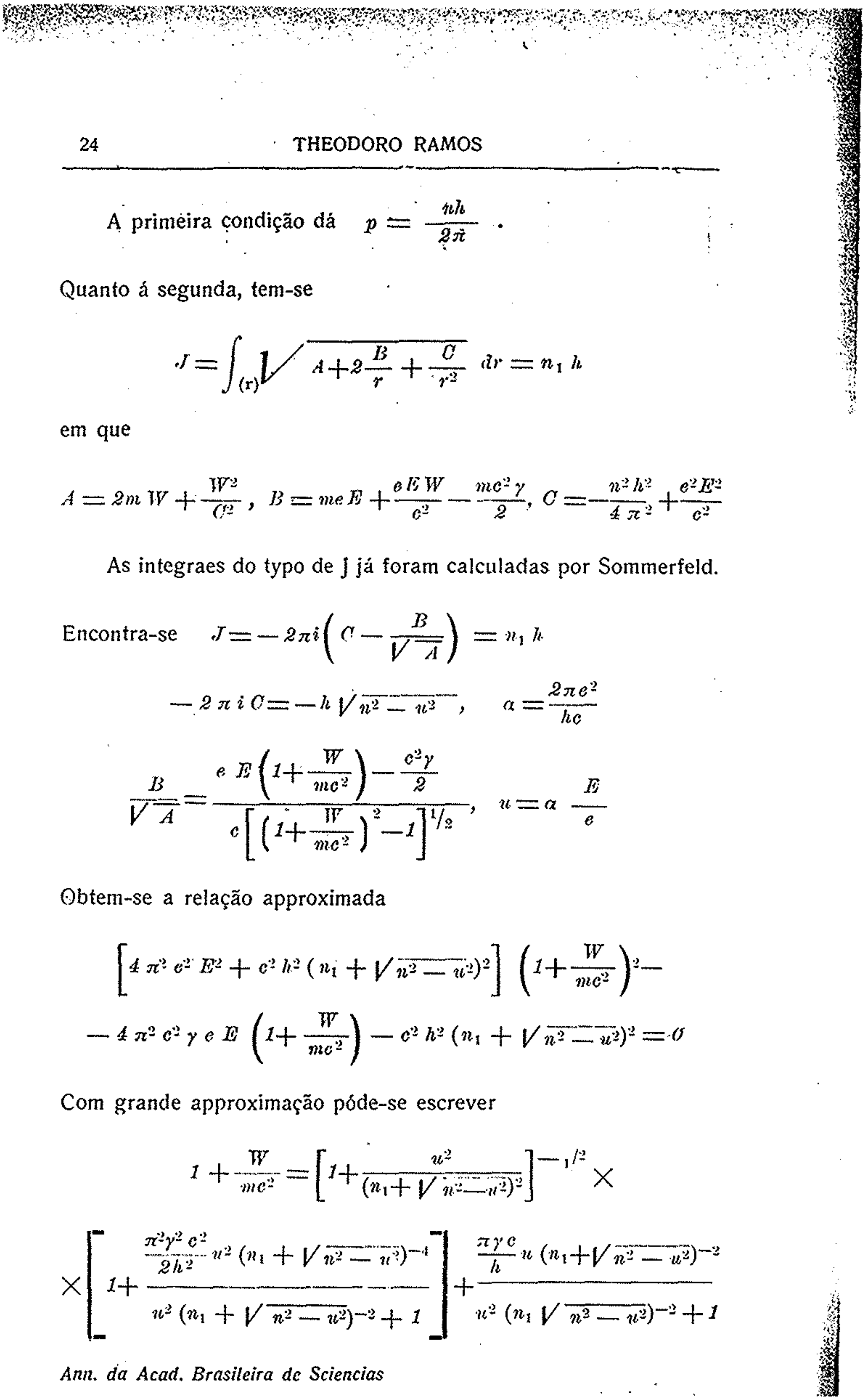
$$p^2_r=\left(2m\,W+\frac{W^2}{c^2}\right)+2\left[me\,E+\frac{e\,E\,W}{c^2}-\frac{mc^2\gamma}{2}\right]\frac{1}{r}+$$

$$+\left[\frac{e^2E^2}{c^2}-p^2\right]\frac{1}{r^2}$$

As condições de estabilidade da trajectoria são

$$\int_{(\varphi)}p_\varphi\,d\varphi=nh\,,\qquad\int_{(r)}p_r\,dr=n_1h$$

em que n e n_1 designam 2 numeros inteiros e h é a constante universal de Planck. As integrações devem ser extendidas á todo o dominio de variação de φ_r e de respectivamente.



A primeira condição dá $p = \frac{nh}{2\pi}$.

Quanto á segunda, tem-se

$$J = \int_{(r)} \sqrt{A + 2\frac{B}{r} + \frac{C}{r^2}}\, dr = n_1 h$$

em que

$$A = 2m W + \frac{W^2}{C^2}, \quad B = m e E + \frac{e E W}{c^2} - \frac{m c^2 \gamma}{2}, \quad C = -\frac{n^2 h^2}{4\pi^2} + \frac{e^2 E^2}{c^2}$$

As integraes do typo de J já foram calculadas por Sommerfeld.

Encontra-se $J = -2\pi i \left(C - \frac{B}{\sqrt{A}} \right) = n_1 h$

$$-2\pi i C = -h \sqrt{n^2 - u^2}, \qquad \alpha = \frac{2\pi e^2}{hc}$$

$$\frac{B}{\sqrt{A}} = \frac{e E \left(1 + \frac{W}{mc^2}\right) - \frac{c^2 \gamma}{2}}{c \left[\left(1 + \frac{W}{mc^2}\right)^2 - 1 \right]^{1/2}}, \quad u = \alpha \frac{E}{e}$$

Obtem-se a relação approximada

$$\left[4\pi^2 e^2 E^2 + c^2 h^2 (n_1 + \sqrt{n^2 - u^2})^2\right] \left(1 + \frac{W}{mc^2}\right)^2 -$$

$$- 4\pi^2 c^2 \gamma e E \left(1 + \frac{W}{mc^2}\right) - c^2 h^2 (n_1 + \sqrt{n^2 - u^2})^2 = 0$$

Com grande approximação póde-se escrever

$$1 + \frac{W}{mc^2} = \left[1 + \frac{u^2}{(n_1 + \sqrt{n^2 - u^2})^2}\right]^{-1/2} \times$$

$$\times \left[1 + \frac{\frac{\pi^2 \gamma^2 c^2}{2h^2} u^2 (n_1 + \sqrt{n^2 - u^2})^{-4}}{u^2 (n_1 + \sqrt{n^2 - u^2})^{-2} + 1} \right] + \frac{\frac{\pi \gamma c}{h} u (n_1 + \sqrt{n^2 - u^2})^{-2}}{u^2 (n_1 \sqrt{n^2 - u^2})^{-2} + 1}$$

Desenvolvendo em série os radicaes, vem

$$\left[1+\frac{u^2}{(n_1+\sqrt{n^2-u^2})^2}\right]^{-1/2}=1-\frac{1}{2}\frac{u^2}{(n+n_1)^2}-$$

$$-\frac{1}{2}\frac{u^4}{(n+n_1)^4}\left(\frac{1}{4}+\frac{n_1}{n}\right)+\ldots\ldots$$

$$\frac{\frac{\pi^2\gamma^2c^2}{2h^2}u^2(n_1+\sqrt{n^2-u^2})^{-4}}{u^2(n_1+\sqrt{n^2-u^2})^{-2}+1}=$$

$$=\frac{\pi^2\gamma^2c^2}{2h^2}\left[\frac{u^2}{(n+n_1)^4}+\frac{2n_1+n}{n(n+n_1)^6}u^4+\ldots\right]$$

$$\frac{\frac{\pi\gamma c}{h}u(n_1+\sqrt{n_2-u_2})^{-2}}{u^2(n_1+\sqrt{n_2-u_2})^{-2}+1}=$$

$$=\frac{\pi\gamma c}{h}\left[\frac{u}{(n+n_1)^2}+\frac{u^3}{(n+n_1)^4}\frac{n_1}{n}+\ldots\right]$$

A frequencia ν da radiação emittida (ou absorvida) quando o electron passa de uma orbita á qual corresponde a energia W_k para outra á qual se refere a energia W_n é dada pela equação de Planck-Einstein

$$h\nu = W_k - W_n$$

Vem

$$\nu = [n, n_1] - [k, k_1]$$

em que

$$[n, n_1] = R\,\frac{E}{e}\left\{\left(\frac{E}{e}-\frac{2\pi\gamma c}{h\,a}\right)\frac{1}{(n+n_1)^2}-\right.$$

$$\left.-\frac{2\pi\gamma c}{h}\,\frac{E}{e}\,\frac{a}{(n+n_1)^4}\,\frac{n_1}{n}+\frac{a^2}{(n+n_1)^4}\left(\frac{E}{e}\right)^3\left(\frac{1}{4}+\frac{n_1}{n}\right)+\dots\right\}$$

$$R=\frac{2\pi^2 m e^4}{h^3}$$

Vê-se que o termo achado por Sommerfeld

$$R\left(\frac{E}{e}\right)^2\frac{1}{(n+n_1)^2}+\frac{1}{4}\,\frac{a^2 R}{(n+n_1)^4}\left(\frac{E}{e}\right)^4$$

soffre uma diminuição cuja parte principal é dada pela quantidade

$$-\frac{2\pi\gamma c}{h\,a}\,R\,\frac{E}{e}\,\frac{1}{(n+n_1)^2}\,.$$

Quanto ao termo que rege a estructura do "doublet", soffre tambem uma diminuição correspondente a

$$-\frac{2\pi\gamma c}{h}\,a\,R\left(\frac{E}{e}\right)^3\frac{n_1}{n}\,\frac{1}{(n+n_1)^4}\,.$$

A correcção do termo principal representa, para o hydrogenio, uma fracção do termo de Sommerfeld $\frac{1}{4}\,\frac{a^2 R}{(n_1+n)^4}$ da ordem de grandeza de $\frac{\gamma c}{h\,a^3}$ ou 10^{-7} (1), e não póde, portanto, ser, actualmente, submettida ao "contrôle" experimental.

---

(1) Adoptando para as constantes os valores que se acham na obra de Sommerfeld, e admittindo com Rutherford que é de 10^{-16} a ordem de grandeza do raio do nucleo positivo.

Quanto á correcção relativa á estructura do "doublet", ella é uma fracção da ordem de 10^{-12} do termo correspondente achado por Sommerfeld; trata-se, pois, de uma modificação desprezivel. E', entretanto, interessante constatar que Paschen em suas experiencias achou para o afastamento do "doublet" do hydrogenio um valor ligeiramente inferior ao que foi calculado por Sommerfeld. A experiencia confirma, pois, uma correcção tendo o mesmo sentido da que achamos; a ordem de grandeza é, porém, differente.

Terminando esta nota assignalaremos que o estudo da orbita do electron póde ser effectuado com o auxilio das funcções ellipticas. A variavel φ é dada em funcção de r por uma integral que contém um radical do 4.º grão em $\frac{1}{r}$ (2).

Sessão de Novembro de 1923.

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(2) Em um campo de Schwarzschild encontra-se um radical do 3.º grão.

T. 1, n.º 1, Março de 1929

Theodoro Ramos approached the problem from the point of view of the general theory of relativity. It is a rather complex mathematical treatment that analyzes the movement of the electron around the nucleus and it involves differential equations with seven coordinates (r, θ, φ, ρ_r, ρ_θ, ρ_φ, t). Since the development is essentially mathematical, we reproduced the original article in entirety in Portuguese.

As can be seen from the analysis of the treatment, the results obtained by Theodoro Ramos explained a little better the splitting of the doublet and represents an improvement of the Bohr-Sommerfeld model of the atom.

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EXTRACTION OF HEAVY METALS IN A SEWAGE SLUDGE-TREATED LATOSOL

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ABSTRACT: *The presence of heavy metals is one of the main hazards against the use of sewage sludge in agronomy. In a field experiment applications of sewage sludge in medium textured Dark Red Latisol (DRL) were evaluated by the extraction of essential or non-essential metals with a DTPA extractor. Experimental design consisted of randomized blocks subdivided in sections of 6 treatments of sewage sludge (0, 6, 20, 40, 60 and 80 t ha^{-1}) during the first year and (0, 6, 20, 40, 60 and 80 t ha^{-1}) during the second year. The experiment had 4 replications and 5 soil collection periods (0, 30, 60, 90 and 120 days of sludge incorporation). Sewage sludge was applied at a mean depth of 0–20 cm. Soil sampling was undertaken during the periods of sludge incorporation so that the elements available in the soil in different doses could be evaluated. Soil samples were analyzed as to fertility level. Concentrations of the metals Cu, Zn, Cd, Ni, Co, Pb and Cr were determined by atomic absorption in DTPA extractor solution. Concentrations of Cd, Ni, Co, Pb and Cr were not detected since values were lower than the detection limit of each. Application of sewage sludge increased Cation Exchange Capacity (CEC) and there was an initial pH variation, albeit the latter returned concentration to its original level. Owing to the repetition of applied sludge, Cu and Zn rates in soil samples gradually increased during the two agricultural years caused by an increase in the doses of applied sewage sludge.*

Key words: heavy metals; biosolid; DTPA; availability of nutrients.

RESUMO: *Um dos principais motivos da insegurança na utilização agronômica do lodo de esgoto é a presença de metais pesados. Desta forma, em experimento em campo, foram avaliados os efeitos de aplicações deste lodo num Latossolo Vermelho distrófico (LVd) de textura média mediante a extração de metais (essenciais e não) pelo extrator DTPA. O delineamento experimental foi o de blocos casualizados, em parcelas subdivididas no tempo constituídas por seis tratamentos de lodo de esgoto (0, 6, 20, 40, 60 e 80 t ha^{-1}) no 1^{0} ano agrícola e (0, 20, 40, 60 e 80 t ha^{-1}) no 2^{0}. O experimento teve 4 repetições e cinco épocas de coleta de solo (0, 30, 60, 90 e 120 dias da incorporação do lodo). O lodo de esgoto foi aplicado numa profundidade média de 0 - 20 cm. Nos períodos (dias) previstos foi feita a amostragem de solo para fins de avaliação dos elementos disponíveis. As amostras de terra foram analisadas com relação ao nível de fertilidade. As concentrações dos elementos Cu, Zn, Cd, Ni, Co, Pb e Cr foram determinadas pelo método da absorção atômica na solução obtida com o extrator DTPA. As concentrações dos metais Cd, Ni, Co, Pb e Cr não foram detectadas por se encontrarem abaixo do respectivo limite de detecção do método. A aplicação de lodo de* *esgoto causou aumento na CTC, e uma variação inicial do pH que após manteve-se próximo ao inicial. Foi possível concluir que, com a repetição da aplicação lodo, os teores de Cu e Zn nas amostras de solos aumentaram gradativamente nos dois anos agrícolas, com o aumento das doses do lodo aplicado.*

INTRODUCTION

Society is increasingly aware of preserving and protecting the environment, especially the water body, the basis of life on the planet. Although sewage treatment should come prior to its disposal, this rule is rarely accomplished[1].

Sewage treatment produces sewage sludge made up of organic matter and mineral components including heavy metals. Disposal of sludge is a matter of great importance due to the possibility of the presence of heavy metals and pathogens that may pollute the environment if not properly treated. The agricultural recycling of sewage sludge is currently one of the best alternatives for its disposal when the necessary requirements related to concentrations of pollutants and pathogens are attended to. Since high fluctuations in the composition of these concentrations exist and there are several difficulties to foresee the behavior of some metals in certain types and qualities of soil, some criteria should be adopted with regard to these restricting factors, including the application of high doses of residues[2].

Organic matter added to the soil improves its physical, chemical and biological qualities. In proper conditions (for example, in aerobic conditions) it undergoes mineralization and releases mineral components in their highest oxidation states, such as, CO_2, H_2O, NO_3^-, SO_4^{2-}, PO_4^{3-} and metals coupled to them. Organic matter disappears after a certain period of time and more is needed to improve soil conditions. There is, however, great concern with regard to the environmental safety needed for the feasibility of the practice when successive applications of sewage sludge are made. Depending on their rates, heavy metals accumulated by applications and soil conditions may be available to plants at phytotoxic levels. They will negatively affect the plant development, possibly transfer them to the food chain, with damaging results to the consumer's health[3] and contaminate surface and sub-surface water through erosion and percolation.

As a rule, home-originated biosolids have less metal concentration than those from industrial discharges. Actually, the origin and the treatment process affect the characteristics of these discharges.

The behavior of heavy metals in the soil after the end of the application of biosolids is unknown. Heavy metals may be adsorbed in the soil through specific or non-specific adsorption reactions. Iron oxides and organic matter are among the components that most retain heavy metals. pH, CEC and cations affect adsorption and the type of ions of heavy metals in the soil. Metals may be found as free ions in solutions or they may constitute compounds with organic and inorganic links. The free types are more important in environmental pollutant studies since they are immediately bioavailable[4,5].

Heavy metal contamination in soil treated with town residues is frequently assessed by their total concentration in the soil. Total metal content in the soil is not a good criterion to foresee phytoavailability[6]. Nevertheless, total concentrations aim at furnishing data on the accumulation of these elements through a certain period of time.

Laws that monitor levels of heavy metals in biosolids and maximum concentration in soils fail to give clear indications. However, phytoavailable concentrations should be known when effects on plants and on food chain are involved[6].

Most methods that determine the availability of metals in the soil are based on the extraction of the specific element by a solution that imitates the plant's course of action. Quelant agent DTPA-TEA has also been used in certain studies of the extraction of heavy metals, others besides Cu, Mn and Zn, according to original suggestion by Lindsay & Norwell (1974)[7], in several types of biosolid-treated soils[8,9,10]. There are certain difficulties to define an extractor that would simultaneously process several heavy metals and be efficient enough to diagnose their availability in different vegetation species cultivated in several types of soils. In the case of sludge interruption doubts still exist with regard to the availability of these elements when the residue's organic change degenerates and the soil's acidity increases. The need for more research is urgently felt, especially when conditions peculiar to Brazil are taken into consideration.

Keeping in mind the verification of parameters for the application of sewage sludge in soils, the present research aims evaluating results of successive applications of sewage sludge on pH and CEC variations and the availability of these heavy metals in the soil.

MATERIALS AND METHODS

General characteristics of site, soil and sludge

The experiment was undertaken on the Experimental Farm of the State University of Maringá, in the Iguatemi district, municipality of Maringá PR Brazil, 23° 25'00" S and 51° 25'00" W, 555 m above sea level, with slightly hilly relief, during the agricultural years 2000-2001 (agricultural first year) and 2001-2002 (second year). Soil belongs to the dystrophic Dark Red Latisol group with average clayey texture. Rates of fine and thick sand, silt and clay were 570, 280, 20 and 130 g kg^{-1}, respectively.

Sewage sludge was obtained from the Sewage Treatment Station, STS-01, of the Paraná Water Works (SANEPAR), in Maringá. Sewage sludge, matured and stocked in the open air, naturally humid and limeless, was solid at the time of collection. A sample to determine its humidity and chemical characteristics was taken. Three aliquots of the sample were removed to determine their humidity. They were dried in a buffer at 65 °C till the formation of a constant mass. Humidity was determined by difference of mass[11]. Thus the amounts of humid sewage sludge necessary for distribution in each experimental unit were calculated and doses for the different treatments to be applied in soil were obtained.

Aliquots of 10 g of recently collected *in natura* sewage sludge were obtained to determine their pH, according to technique developed by Andreoli & Bonnet[11].

For the chemical characterization of sewage sludge, the dried aliquots were mixed, ground, homogenized, sieved and the resulting sample treated to a constant mass. For the determination of nutrient and non-nutrient metals, 0.5000 g of aliquots from sample were then decomposed, by a wet method, with a nitro-perchloride mixture, in a digestor block. Metal concentrations were determined by the atomic absorption flame-type method[12]. Kjeldahl method was used for nitrogen (N) determination and the gravimetric method of thermal decomposition was used to determine organic matter (OM)[13]. Whereas Table 1 shows results, Table 2 gives results for heavy metals used in the current analysis.

Table 1. Mean rates of chemical parameters of sewage sludge used in experiment, associated to soil fertility (†).

Sewage sludge	N	C	OM	C:N	Mn	Cu	Zn	Fe	pH(‡)
	←	g kg^{-1}		→	←	mg kg^{-1}		→	
1st application	37.0	264.0	405.0	7:1	274.1	480.0	1320.0	42800.0	4.68
2nd application	32.2	235.8	406.5	8:1	298.0	450.00	1540.0	48600.0	4.72

(†) – Analyses were undertaken in the Agro-Chemical and Environment Lab of UEM. (‡) - pH rates were measured in the original material and the others in dry material at 65°C. OM – Organic Matter.

System of Experiment

Field experiment was designed in randomized blocks with four repetitions each. Sewage sludge doses consisted of 0, 6, 20, 40, 60 and 80 t ha^{-1}. Sampling periods were 0 (blank), 30, 60, 90 and 120 days of sludge incorporation to soil, respectively. Each block consisted of 6 experimental units. Experimental unit referring to each sludge dose was made up of five 23 m-long rows (with maize plants), space 1.0 m and 0.20 m between plants, with total area 5 m x 23 m = 115 m^2. Real unit area was 3 m x 20 m = 60 m^2.

Sewage sludge was applied on the surface of the area; spreading was made with spades and hoes; incorporation occurred by harrowing at approximately 0–20 cm depth, equally in both applications.

Table 2. Concentration of heavy metals without any essential trait for plants in the sewage sludge used in soil treatments (†).

Sewage sludge	Cd	Ni	Cr	Co	Pb
	←		(µg g^{-1})		→
1st application	2.8	88.0	72.5	72.5	492.0
2nd application	2.1	142.0	125.0	125.0	380.0

(†) – Analyses were undertaken at the Agro-Chemical and Environment Lab of UEM.

Collection, preparation and analysis of soil samples

Collection of soil samples of each experimental unit, corresponding to 5 treatments and control, of each randomized block, at 0-20 cm deep, was undertaken at 0, 30, 60, 90 and 120 days of sewage sludge incorporation, for each agricultural year. A sample composed of 4 simple samples resulted from each experimental unit. Collected compound samples were identified, air dried, sieved in 2 mm-mesh polypropylene sieves, homogenized and stored as ADFE (Air-Dried Fine Earth).

Analysis for Soil Characterization

ADFE samples were routinely analyzed to determine traditional parameters: pH, potential acidity, concentrations of C, N, P, K, Ca, Mg and S, according to IAPAR techniques[14]. Table 3 shows results for treatment-less soil samples for 0 days of incorporation.

Table 3. Chemical characterization of soil used in experiment.

Soil (0-20 cm)	pH $CaCl_2$	P	S	N	C	Ca	Mg	K	H^++Al^{3+}	CEC	SB	C:N	V%
		←mg dm^3→		← g kg^{-1}→		← cmol$_c$ kg^{-1} →							
DDRL	5.0	1.8	6.6	0.6	7.6	3.58	0.88	0.08	3.42	7.96	4.54	12:1	57.0

dDRL – Dystrophic Dark Red Latisol; [H^+ + Al^{3+}] – potential acidity; CEC – Cation Exchange Capacity. Results are mean of analyses with two repetitions.

Analysis of total metal rates in soil

Total rates of metals in soil were determined by interpreting respective concentrations and by atomic absorption technique in the solution from the decomposition of samples obtained by wet method, using a mixture of HNO_3 and $HClO_4$[13].

Analysis of metal rates available in soil

Soluble rates of metals, or rather, the rates available for plants in the soil solution, were determined by the respective metal concentrations of the atomic absorption technique in the solution obtained from the extraction of 20.0000 g of ADFE with 40 mL of the extracting mixture formed by DTPA (Diethylenetriaminepentaacetic acid) 0.005 mol L^{-1} + TEA (triethanolamine) 0.1 mol L^{-1} + $CaCl_2$ 0.01 mol L^{-1}, corrected at pH 7.3[15]. Table 4 shows mean rates of three analytic repetitions for the elements under analysis.

Statistic analysis

The conventional method was used to analyze parts subdivided by periods. The surface response methodology was adopted for regression analysis as from the quadratic polynomial model with two independent variables, according to equation [02][16].

$$Yi = B_o + B_1N_i + B_2T_i + B_3N_i^2 + B_4N_iT_i^2 + B_5N_iT_i + E_i \qquad \text{)2]}$$

where Y_i = variable responses; N_i = biosolid levels; T_i = time levels; E_i = randomized error; B_i with i = 0,1,2,. .,5 = parameters to be assessed.

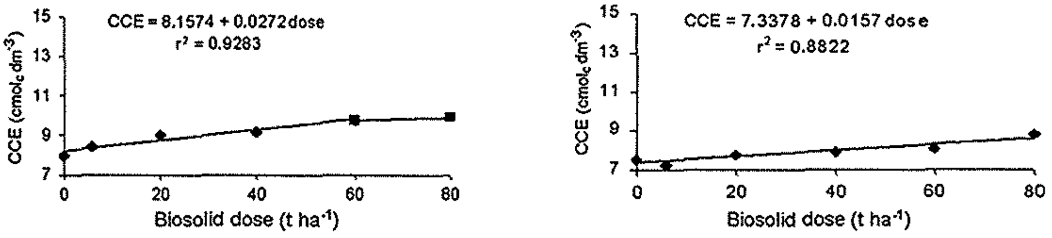
From the complete model above, the equation that best adjusted itself to data was based on the coefficient of determination (CD), represented by r^2, and on the regression coefficient by Student's *t* test (up to 10% probability) and by the analysis of residues. Since only three evaluations were done during the second agricultural year, the result was equation [03]

$$Y_i = B_O + B_1N_i + B_2T_i + B_3N_i^2 + B_4N_iT_i^2 + E_i \qquad [03]$$

RESULTS AND DISCUSSION

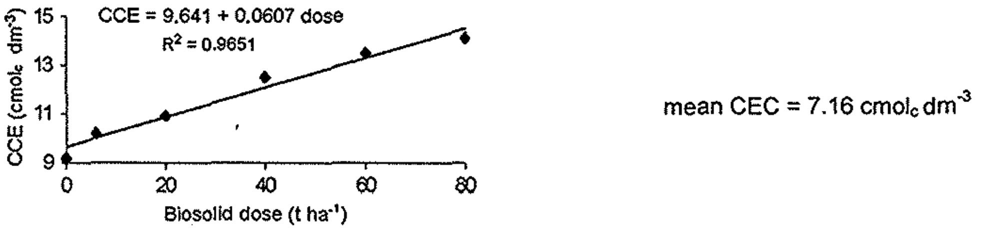
Cation Exchange Capacity (CEC) and pH

Regression analysis showed that the applied sewage sludge dose is significantly related to the soil's CEC (Figure 1 (a) $r^2 = 0.9283$; (b) $r^2 = 0.8822$; (c) $r^2 = 0.9651$). Variance analysis indicated that during the two agricultural years significant results occurred only in sewage sludge doses. There was an increase in CEC as a result of residue doses during these years (Figure 1). The variable CEC increased linearly in the first agricultural year (2000-2001), Harvest 1 and 2, and during the second year (2001-2002), Harvest 3. However, during the second year (2002), Harvest 4 failed to show any significant treatment results: mean was 7.16 $\text{cmol}_c\ \text{dm}^{-3}$.



(a) Harvest 1

(b) Harvest 2



(c) Harvest 3

(d) Harvest 4

Figure 1. Cation Exchange Capacity (CEC) of soil during agricultural years 2000-2001 and 2001-2002, Harvests 1 (a), 2 (b), 3 (c) and 4 (d), as a result of increasing dose of sewage sludge.

CEC increase, as a result of residue doses, showed a linear behavior within the samples (Figure 1). There was a rising linear trend in the variable under analysis: 0.0272 cmol$_c$ dm^{-3} were added to the soil for each dose of 80 t ha^{-1} of applied residue. Research showed CEC increase when sewage sludge was applied[17, 18]. In fact, the above authors have reported increasing CEC when sewage sludge was applied in doses ranging between 0 and 240 t ha-^{1} (dry base).

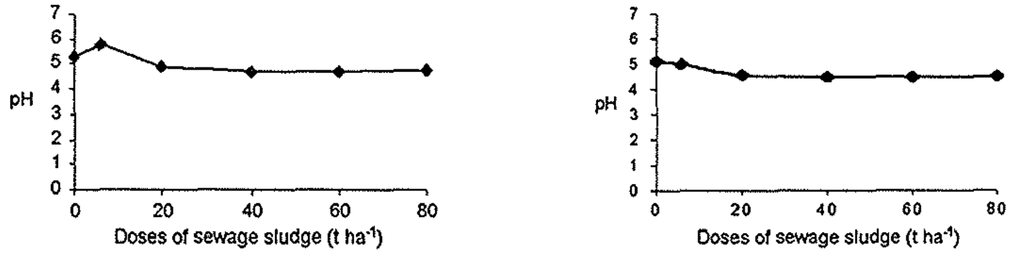
Increase of soil's CEC, resulting from a rise in sludge dose, is normal. Organic matter has active sites with a capacity for linking and exchanging ions according to pH. Carboxylic, phenolic, carbonylic, alcoholic, amminic groups are among the active sites directly proportional to the amount of organic matter that has been stabilized by mineralization.

Figure 2 shows the behavior of pH as a result of increasing doses of sewage sludge applied to soil. There was a pH increase up to 6 t ha^{-1}; pH stabilized for other doses in Harvest 1. During the same year, in Harvest 2 there was a decrease in pH when residue doses increased. There was a decreasing trend in the effect of residue on the soil's pH, which stabilized during harvest and maintained itself close to the initial value.

Mineralization of sewage sludge in an aerobic environment oxidizes C, N, and S to the higher oxidation state. Carbonic acid, H_2CO_3, nitric acid, HNO_3, and sulfuric acid, H_2SO_4 are formed. However, in a water solution, they dissociate and form protons which cause a decrease in pH. Logan et al. (1997)[19] reported a decrease in pH rate for the smallest sewage doses 7.5 and 15 t ha^{-1} in soil from calcareous rocks during the first year of limeless sludge application. The authors accounted acidification to reactions of nitrification of the residue's ammoniacal nitrogen.

Oliveira (2000)[20] and Bertoncini & Mattiazzo (1999)[21] reported an increase in pH rates when increasing doses of biosolid were added. According to these author, pH increased due to alkalinity of material used. Discrepancy in results must be linked to the different characteristics of sewage sludge in different experiments.

During the second year (Harvests 3 and 4, Figure 2) no significant effect on pH occurred as a result of levels of applied sludge and culture period. Mean pH was 4.40 and 4.35 respectively.



(a) Harvest 1

(b) Harvest 2

Mean pH = 4.40

(c) Harvest 3

Mean pH = 4.35

(d) Harvest 4

Figure 2. Mean pH rates in soil during agricultural years 2000-2001 and 2001-2002, in Harvests 1(a), 2 (b), and mean pH in Harvests 3 (c) and 4 (d), as a result of increasing doses of sewage sludge.

Heavy metals (non-essential elements): Cd, Cr, Ni, Co and Pb

According to Table 2, atomic absorption method, flame-mode, revealed heavy metals Cd, Cr, Ni, Co and Pb in sewage sludge when total decomposition of sample occurred with nitric-perchloric mixture. However, when soil with doses 0, 6, 20, 40, 60, 80 t ha^{-1} of sewage sludge (corresponding to the different treatments) was extracted by DTPA-TEA, these elements failed to be detected since their concentration was below the method's detection limit.

Oliveira (1995)[9] and Bertoncini (1997)[10] did not report removal of Cr by DTPA extracting solution. Anjos (1999)[22] analyzed Dark Red Latisol and Red Latisol treated with different sludge doses, totaling 388 t ha^{-1} (dry base), and found that Cd and Pb concentrations, assessed by extractor DTPA-TEA, were lower than the method's detection limit. In field work Oliveira (2000)[20] evaluated the phytoavailability of heavy metals in a Red Latisol treated with 33, 66 and 99 t ha^{-1} of sewage sludge (dry base) during the first year, and with 37, 74 and 110 t ha^{-1} (dry base) during the second year. The above mentioned researcher reported that Cd, Cr and Pb rates, evaluated by three extractors, including DTPA-TEA, were below the detection limit of the analytic method. Simonete (2001)[23] found that in a Red Agrisol treated with 0, 10, 20, 30, 40 and 50 t ha^{-1} of sewage sludge (dry base), in a hot house, rates of Cd, Ni, Pb and Cr, extracted by DTPA-TEA, were below the method's detection limit for all treatments.

Evaluation of available rates of Cu and Zn in soil

Cu and Zn amounts removed from soil samples by extractor solution increased according to sewage sludge doses which were applied, or rather, $Zn^{2+} > Cu^{2+}$. The above shows current rates in sewage sludge (1320.0; 480.0 and 1540.0; 450.0 mg kg^{-1}, respectively) and respective doses incorporated to soil (Table 4).

Table 4. Mean rates of Cu and Zn extracted by DTPA-TEA, obtained by analytic results of 5 samples composed of soil collected in 0, 30, 60, 90 and 120 days of biosolid incorporation, according to increasing doses of sewage sludge.

Agricultural	Sewage sludge doses (t ha^{-1})*						
Year	0	6(12)	20(40)	40(80)	60(120)	80(160)	CDD (r^2)
				Copper (mg kg^{-1})			
2000-IE	0.82	1.23	1.89	2.21	2.77	3.12	0.92
2001-RE	0.86	1.49	2.31	2.87	3.63	4.01	0.92
2001-IE	0.91	1.75	3.27	4.91	5.95	6.78	0.88
2002-RE	1.05	2.68	4.76	6.74	7.94	8.93	0.90
				Zinc (mg kg^{-1})			
2000-IE	0.74	1.13	3.78	5.62	7.12	8.19	0.95
2001-RE	0.83	1.82	4.58	6.50	8.36	9.56	0.96
2001-IE	0.81	2.55	6.41	8.97	11.04	13.74	0.92
2002-RE	0.86	3.57	8.45	11.35	14.95	17.35	0.94

* Doses between brackets are for 2001 and 2002; IE: Immediate Effect (1st – 3rd Harvest: conventional); RE: Residual Effect (2nd - 4th Harvest: winter harvest). CD – Coefficient of Determination, r^2.

This fact may be explained by the concentration of the metals in the residue. Mean rate increases of available elements were reported when compared to that of control. They varied from the lowest to the highest dose applied in the harvests, or rather, from 53 to 1007%; 119 to 1052%; 215 to 1596%; 315 to 1917%, respectively, for Zn (Table 4). The above was corroborated by Simonete (2001)[23] who applied sewage sludge in soil cultivated with maize, in a hothouse, and discovered higher rates for iron and zinc. Oliveira (2000)[20] applied sewage sludge to soil with sugarcane and found higher zinc rates when compared to other metals. The high amount of metal in the residue accounted for the increase. However, in this context, copper also contributed towards such increase and varied from 50 to 280%; 73 to 366%; 92 to 645%; 155 to 750%, respectively. The increase was due to high amount of the metal in the sewage sludge.

When amounts of these metals in the soil during the first agricultural year (Harvests 1 and 2) have been taken into account, mean extraction of Cu and Zn were respectively 24% and 20% in treatments with sewage sludge doses by DTPA. During the second agricultural year (Harvests 3 and 4) values were respectively 31% and 21% (Table 4). Cu and Zn rates removed from soil by extractor were, as a rule, significantly affected by doses and periods with an increase in these metals (Figures 3 and 4).

Several authors[20, 22, 24] found results satisfactory for DTPA-TEA and Mehlich-3 for foreseeing availability of Cu and Zn in plants cultivated in soils with sewage sludge. Nevertheless, variations in extractors may exist according to plants under analysis[25].

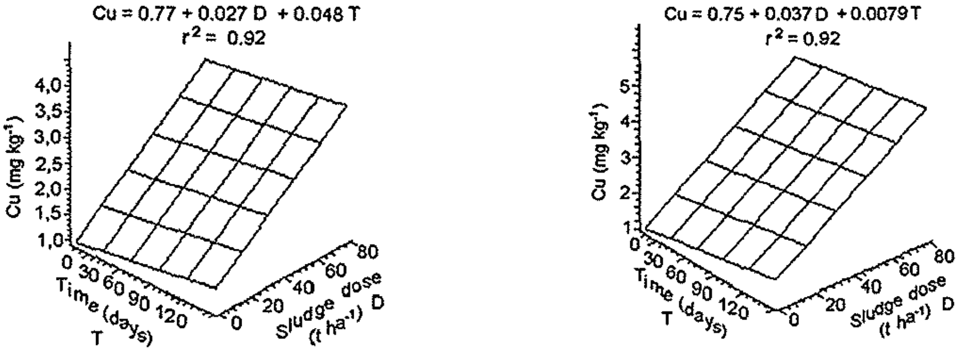
Copper

Variance analysis showed that the availability of copper in the soil was significantly related to sewage sludge doses and sampling periods, although no interaction between these factors has been detected. (Figures 3 a, b). Besides the fact that rate increase due to residue doses and to sampling period had a linear behavior, in the second agricultural year (2001-2002), Harvests 3 and 4, the variables period and doses showed an increasing linear trend of the applied residue (Figures 3 c, d).

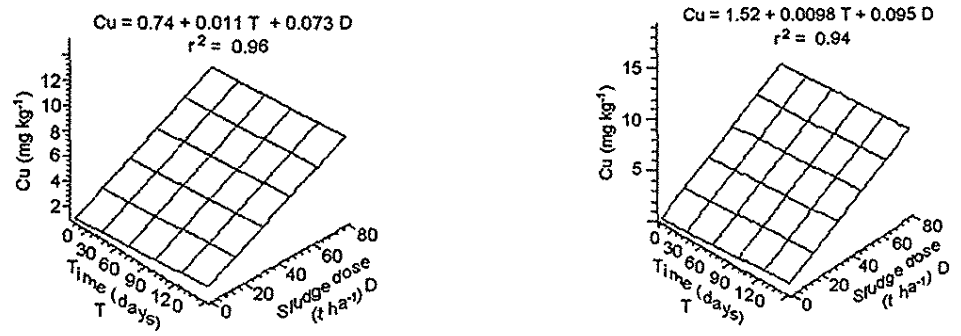
The main link of copper with organic matter lies in humic and fulvic acids, probably forming stable compounds with copper. In some soils copper is associated with insoluble organic material[4] with only a slight mobility. The interaction of copper with humic acids decreases according to the increase of the amount of copper applied[25], it increases according to humification rates[5] and to pH[26]. However, not all organic copper in the soil is insoluble[5]. According to McLaren and Crawford (1973)[27] the copper in soil solution available to plants is replaced by modes weakly associated to organic matter. In field conditions, after 15 years of sludge application[28], it was demonstrated that part of the soluble copper returned in a complex organic mode. Copper availability was affected by the soil's pH and tended to decrease with the latter's rise. Redente and Richards (1997)[29] verified that liming decreases the availability of the element in copper-rich soils.

Zinc

Variance analysis revealed a rising linear trend in zinc between the period and sewage sludge doses applied to the soil for the agricultural year 2000-2001 (Figure 4 a, b).



(a) Harvest 1 (b) Harvest 2

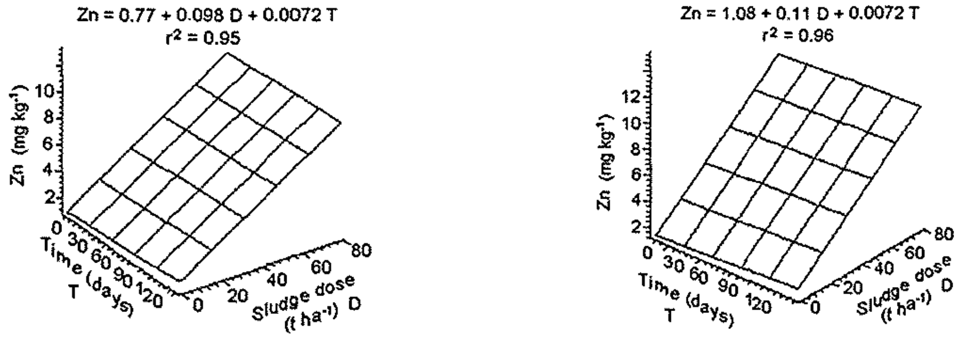


(c) Harvest 3 (d) Harvest 4

Figure 3. Variation of mean rates of Cu (a) Harvest 1, (b) Harvest 2, (c) Harvest 3 and (d) Harvest 4, removed by DTPA pH 7.3 as a result of sewage sludge applications in the four harvests.

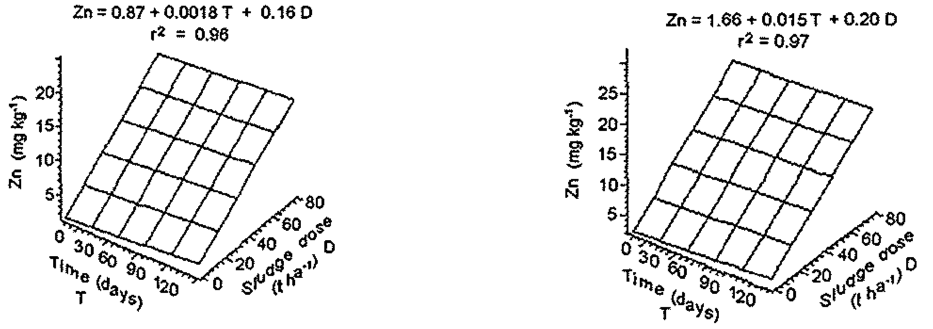
In the second year, 2001-2002, zinc showed a significant rising linear trend according to the period and sewage sludge doses applied to the soil (Figure 4 c, d).

In the second agricultural year availability of zinc was higher in the two harvests due to the cumulative effect of two sewage sludge applications to soil with a high concentration of the element in the residue and a decrease in pH. However, availability of the element decreases when a rise in pH occurs[30]. Machado and Pavan (1987)[31] evaluated zinc adsorption in the soils of the state of Paraná with different pH rates. They concluded that maximum capacity of soil's adsorption and the link energy between the soil and zinc ion increased in proportion to pH rise. Further, adsorption was significantly correlated to pH and CEC.



(a) Harvest 1

(b) Harvest 2



(c) Harvest 3

(d) Harvest 4

Figure 4. Variation in mean rates of Zn (a) Harvest 1, (b) Harvest 2, (c) Harvest 3 and (d) Harvest 4, removed by DTPA pH 7.3, owing to sewage sludge applications in four harvests.

Cunha et al. (1994)[32] concluded that, in soils of the state of São Paulo, pH and CEC of soil were the factors that best explained maximum adsorption of zinc adsorbed to the organic part, by means of an increase in CEC and especially the residual part. Addition of biosolid produced significant increase in Zn (in the three years evaluated). This fact has been detected by all extraction methods, including DTPA at pH 7.3[25].

CONCLUSION

Application of sewage sludge in soil produced simultaneously an increase of CEC in soil and a decrease in pH; later on the latter maintained itself close to start rate.

Heavy metals, non-essential to plants, showed concentrations lower than the detection limit of the analytic method.

Rates of metal in soil gradually increased, in proportion to the increase of doses of sewage sludge applied.

Results of sewage sludge application may be considered as metal sources.

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POLLUTION EFFECTS ON THE ENVIRONMENT, MACROPHYTES AND FISHES IN THE SAPUCAIA STREAM, GUAÍBA HYDROGRAPHIC BASIN, RS, BRAZIL.

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ABSTRACT

This paper shows the results of air, water and sediment quality of Sapucaia stream, which belongs to Guaíba Hydrographic Basin, in the State of Rio Grande do Sul, Southern Brazil. The correlations among the concentrations of Al, Cu, Fe, Mn and Zn, present in the atmosphere, water and sediments, and their bioaccumulation in macrophytes are deteminated. Different degrees of pollution are characterized through the study of the oxidative damage in fishes. The results indicate metal accumulation in macrophytes and fishes.

RESUMO

Este trabalho apresenta os resultados da qualidade do ar, da água e de sedimentos do Arroio Sapucaia, que pertence à Bacia Hidrográfica do Guaíba, Estado do Rio Grande do Sul, Sul do Brasil. São determinadas as correlações entre as concentrações de Al, Cu, Fe, Mn e Zn, presentes na atmosfera, na água e em sedimenentos, e sua bioacumulação em macrófitas. Através do estudo dos efeitos oxidativos em peixes são caracterizados diferentes graus de poluição. Os resultados indicam uma acumulação de metais em macrófitas e em peixes.

KEY WORDS: environmental survey, fishes, macrophytes, micro and macro elements, pollution

INTRODUCTION

The quality of water and air in the Sapucaia Stream area, located in the State of Rio Grande do Sul, Southern Brazil, present several degrees of alterations, which affect the life quality of the local population. In this area, air emissions include inorganic and organic gases and suspended solid particles, mainly heavy metal, released by different sources like industries, vehicle traffic, soil erosion, withdrawal of covering plants.

The Sapucaia stream (Figure 1) crosses, in its initial reaches, low environmental impacted areas. In the pursuing of its course, this impact increases until reaching higher a dammage index in its final course, where it discharge its waters in the Sinos River, a tributary of Guaiba hydrographic basin, the main hydrografic basin of the State, water supplier of the city of Porto Alegre (1,500,000 inhabitants). The diverse regions of this basin present different impacts due to the atmospheric fallout and runoff of residues, reflecting in the quality of water, sediments, living organisms of the stream and human population that inhabits the area of the hydrografic basin[1] .

Vegetation, through air absorption, may accumulate trace elements, which may be transferred to animals and human groups through the trophic chain[2]. This accumulation can increase in some seasons of the year[3].

Alterations in the bioaccumulations of some elements in the macrophytes *Ludwigia sp*, *Ludwigia longifolia* and plants like *Paspalum pumilium* and *Acacia niger*, occur in sediment and water, among other parameters, with variations of pH. Usually, iron concentration is high in acid environment while manganese concentration is low[4].

An ecological evaluation of pollutant effects on organisms must include biological, physico-chemical and toxicological analysis. This implies that an analysis of heavy metals or organic residue effects in water must include a complete study of the abiotic conditions[5]. Data organization concerned with pollution and its effects is necessary for an environmental management program.

In this paper, correlations among the concentrations of five elements present in the atmosphere, water and sediments, with their bioaccumulations in vegetation and fish are evaluated. In a previous work[6] the concentrations of 12 elements in the atmosphere of this area were measured and their correlations with bioaccumulation in water, sediments, plants and fishes were presented.

MATERIALS AND METHODS

Area description. Sapucaia stream, tributary of Sinos River, with a length of 25 km, is located between 29° 45' and 30° 00' LS and 51° 15' and 51° 00' LW, covering an area of 129.57 km^2 in the metropolitan region of Porto Alegre (Figure 1). In upper order reaches, the hydrographic basin presents an area with low populational density and agricultural features where small farming activities of low environmental impact prevail. In intermediate areas, there are urban zones of high populational density and a large number of industries (cement, metal-mechanics, oil refinery, and chemical). In this area, urban solid wastes are deposited causing a high environment impact. Also in this region, two principal highways, namely RS 118 and BR 116, with intense traffic of vehicles (around 120,000 vehicles per day) cross the stream. This region is characterized by a high environmental impact. In the final reaches, near the Sinos River, rice culture areas are observed in both edges of the stream[1].

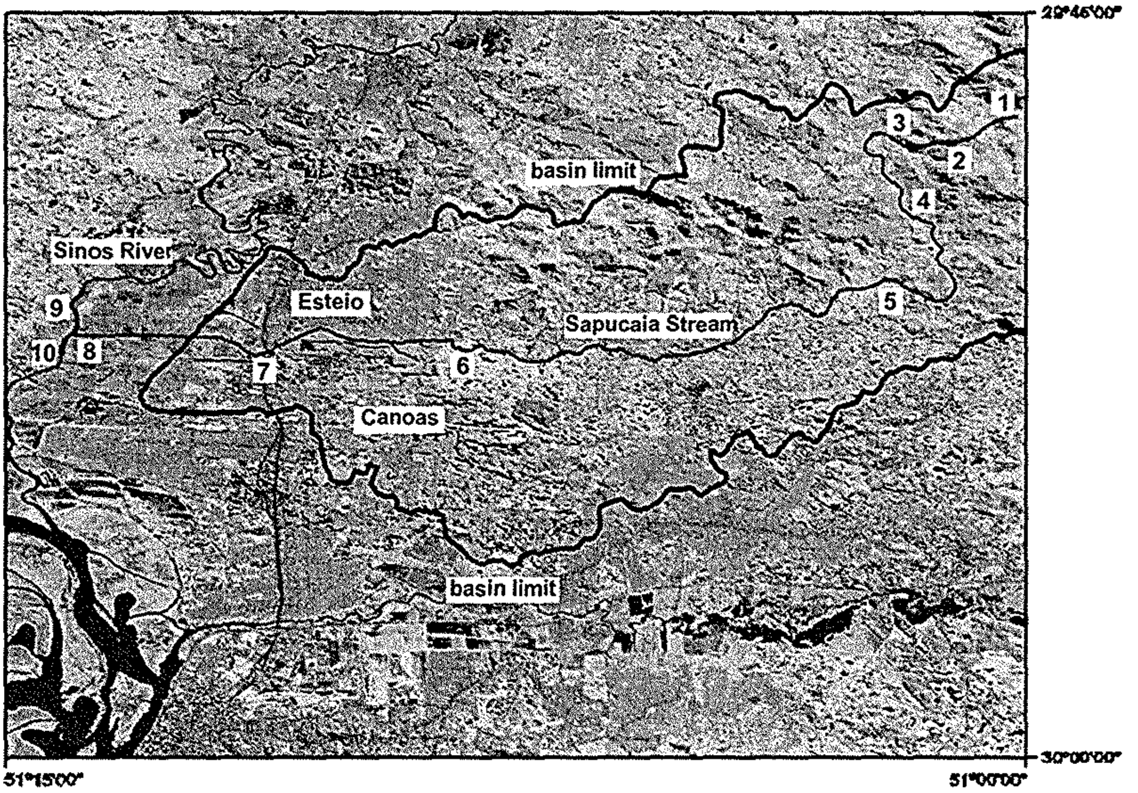

Figure 1. Sampling Points on Sapucaia Stream

Sampling procedures. Eight sampling points were selected in Sapucaia Stream (Figure 1) to collect water, sediment, macrophytes and fishes.

The first was placed near one of the upper level reaches, at 29°49´12,9´´S and 51°49´29,0´´W (135m altitude), in the rural region of Santa Tecla, City of Gravataí, where the environmental impact is relatively low. The second was located at the beginning of a wetland area with cattle breeding activities, at 29° 49´45,9´´S and 51°02´15,7´´W (71m altitude). Sampling point 3 was chosen after the wetland, where the main source of contamination is mining activity (basalt and sandstone-quarry), 29° 49´48,0´´S and 51°02´37,8´´ W (68m altitude). Sampling point 4 was placed in an area with little agricultural activities. In this sampling point, named Sta. Tecla, was placed a high volume sampler (HI- VOL) to collect the total suspended particles (TSP) in the atmosphere, at 29° 50´30.1´´S and 51°02´57.9´´W (altitude 48m).

The fifth point was located after a solid waste deposit facility in Santa Tecla. Afterwards, the stream drains urban areas of the cities of Sapucaia and Esteio cities, with an invader population on the waterfront, at 29° 51´59.1´´S and 51°03´19.4´´W (37m altitude). In the City of Esteio, many industries (including refinery, petrochemical, chemical, cement) and a solid waste recycling plant, which release pollutant materials in the stream, are present. Sampling point 6 was located in this region. Sampling point 7 was located near the highway BR 116, with an intense traffic. Finally, sampling point 8 was placed in the rice culture area just before the Sapucaia stream empties into the Sinos River. Samples were also collected in Sinos River on both sides of the stream mouth (upper head and lower level), to study the interference in Sinos biota (sampling points 9 and 10). Two other HI-VOL samplers were located near to sampling station 6, named Campus, and in a petrochemical plant, named Industrial Zone, (near to sampling station 8).

Water, sediments and macrophytes samples were collected at every sampling point in the cold season (Autumn and Winter, 2001) and in the hot season (Spring, 2001 and Summer, 2002).

Analytical procedures. Analysis of water physical and chemical parameters like pH, saturation percentage and dissolved oxygen (DO), electrical conductivity (EC), hardness, chlorides, alkalinity, organic matter (OM), total nitrogen and phosphorus was made during the year of 2001. The analytical procedures measured five elements (aluminum, copper, iron, manganese, and zinc) content in water. All the determinations were carried according to the Standard Methods present in Standards of American Public Health Association[7].

Analysis of pH and of macro nutrients (nitrogen, total phosphorus and potassium) were performed in dry sediment samples according to Tedesco[8] and Vandecasteele[9].

The HI-VOL samplers operating with a flow rate between 1.1 and 1.7 m^3/min were used to collect total suspended particles in the atmosphere with aerodynamic diameters up to 25-50 µm. Measurements were conducted from March, 2001 to March, 2002.

The filters with the collected particles, after digestion with a 1:1 HNO_3 – HCL mixture (strong digestion), were assayed to determine the concentrations of the chemical elements mentioned before. Mild digestion was used to determine soluble metals in water and in sediments and strong digestion was used to determine total metals in macrophytes and in fishes[3, 10,11].

The analysis of the same elements previously studied in water, air and sediments were performed in a macrophyte, the Commelinaceae *Tripogandra diuretica* and in fishes, Jundiá, *Rhamdia quelen*.

Fish were collected at sampling points 4 and 8, with low and high environmental impacts, respectively, in winter (July, August, 2001) and spring (October, November, 2001). Gills, livers and a piece of muscle of the fishes were collected and were frozen in liquid nitrogen. The samples were kept under dry ice during the transportation to the laboratory. After, the tissues were tritured and blended with a phosphate buffer and centrifuged with 3000 rpm for 10 min at 2° C. Some aliquots of the supernatant material were removed for the TBARS (reactive substances to the thiobarbituric acid) determinations and protein measurements[12]. A statistical analysis was carried out using the "t" Student Test, with 5% for the significance level.

RESULTS AND DISCUSSIONS

The measured pH indicates that, in both seasons, water was slightly basic in the sampling points 1 to 8, and almost neutral in sampling points 9 and 10 (Tables 1 and 2). For the sediments, pH was nearly neutral, except at the points 4 and 5, where it is nearly acid. The sediments were almost neutral at the sampling points 1, 3 and 8 (Tables 1 and 2).

Dissolved oxygen (DO) was very low, even near to the head stream, especially in the cold season (Table 1). During the hot season, the thinner water blade leads to an increase of the concentration of organic mater, resulting in the decrease of the DO concentrations, especially at point 2, wetland areas, and in the final reaches. At sampling points located in areas with great environmental impact, from 4 to 10, very low values for DO were found, when compared to the points near the head stream. The fluctuation of the DO values is linked to the release of pollutants (waste water, industrial sewage) from the urban and the industrial areas.

The higher values of alkalinity, at the head stream points, decrease at the intermediate regions and again become high near the mouth zone (Tables 1 and 2). Phosphorus, electrical conductivity, organic matter and chlorides show a regular increase from the head steam to the mouth zones. Hardness and total nitrogen show great variability among the points(Tables 1 and 2).

Interference in the water quality of Sinos River is indicated by the alterations of the physico-chemical parameters from sampling point 9 (located in the Sinos river, in the upper level of the stream mouth) to point 10 (located in the lower level of the stream mouth).

The geometric means, maximum and minumum values for the total suspended particles (TSP) are shown in Figure 2.

The maximum values for the TSP concentrations were found in the cold season. This is explained by the thermal inversions characteristic of the atmospheric conditions. Also the prevailing wind direction (northwest) in the winter brought the emissions from a metallurgic industry, located northwest of the intermediate sample point, in the hydrografic basin area. The maximum acceptable value[13] for the geometric means of TSP is 80 μg/m^3.

Table 1. Average physico-chemical parameters for water and sediment for cold season (winter and autumn, 2001).

Sampling points	Water								Sediment	
	pH	Dissolved Oxygen (mg/l)	Conductivity (mS.cm^{-1})	Hardness (ppm)	Alkalinity (ppm)	Chloride (ppm)	Organic Matter (ppm O_2)	Total P (ppm)	pH	Total N (ppm)
1	7.75	5.3	0.12	42.89	51	Nd	0.96	0.06	7.00	2.73
2	7.70	7.4	0.12	32.99	41	Nd	2.56	0.12	6.60	7.35
3	7.75	5.8	0.14	54.86	60	Nd	1.28	0.09	7.10	-
4	7.54	3.2	0.12	37.90	48	Nd	0.32	0.08	5.83	11.55
5	7.18	3.0	0.48	32.25	32	Nd	0.24	0.13	5.85	7.00
6	7.40	3.1	0.99	25.94	32	Nd	0.32	0.14	6.58	9.80
7	7.44	2.1	0.38	43.88	87	3.5	0.64	0.83	6.52	12.60
8	7.70	1.8	0.45	58.85	85	4.5	0.48	0.74	7.01	19.25
9	7.04	2.0	0.11	30.92	39	Nd	0.28	0.19	6.50	38.50
10	7.04	3.2	0.21	33.91	53	1.0	0.41	0.26	6.59	16.25

Nd.- not determined

Table 2. Average physico-chemical parameters for water and sediment for hot season (spring, 2001 and summer, 2002)

Sampling points	Water								Sediment	
	pH	Dissolved Oxygen (mg/l)	Conductivity ($mS.cm^{-1}$)	Hardness (ppm)	Alkalinity (ppm)	Chloride (ppm)	Organic Matter (ppm O_2)	Total P (ppm)	pH	Total N (ppm)
1	7.35	3.3	0.21	55.83	71	Nd	1.04	0.09	7.25	17.50
2	6.30	2.1	0.11	37.89	45	Nd	3.92	0.24	7.20	50.75
3	7.20	4.3	0.12	50.85	61	Nd	0.96	0.18	7.54	7.00
4	7.20	5.4	0.11	40.88	51	Nd	2.16	0.34	6.58	8.75
5	7.15	4.1	0.23	44.87	66	1.51	5.12	0.35	6.96	19.25
6	6.85	3.5	0.19	32.9	39	1.76	3.84	0.28	7.23	7.00
7	6.60	3.6	0.19	36.89	52	1.99	4.48	0.61	7.52	10.50
8	7.00	3.2	0.21	37.89	53	2.24	4.21	0.82	7.21	138.25
9	7.00	3.3	0.20	38.10	42	1.86	3.12	0.33	6.42	19.25
10	6.85	3.4	0.13	38.88	36	1.74	3.34	0.51	6.20	7.00

Nd.- not determined

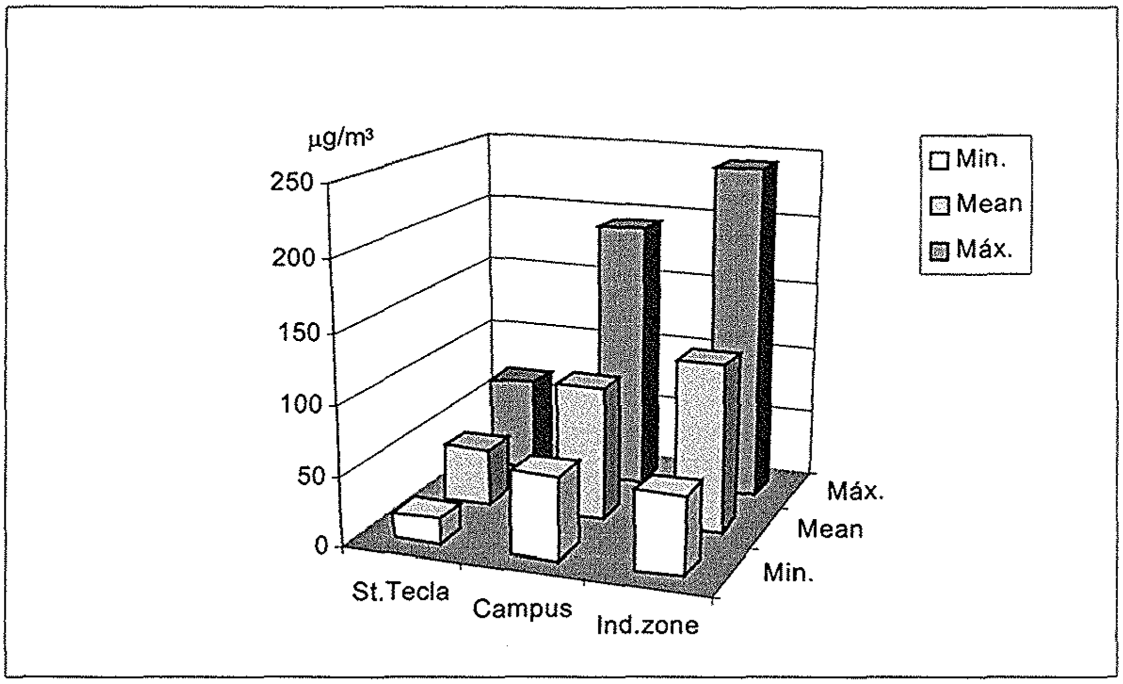

Figure 2. Total suspended particles concentrations in the atmosphere

Figures 3 and 4 show the most representative values for the elements present in the atmosphere.

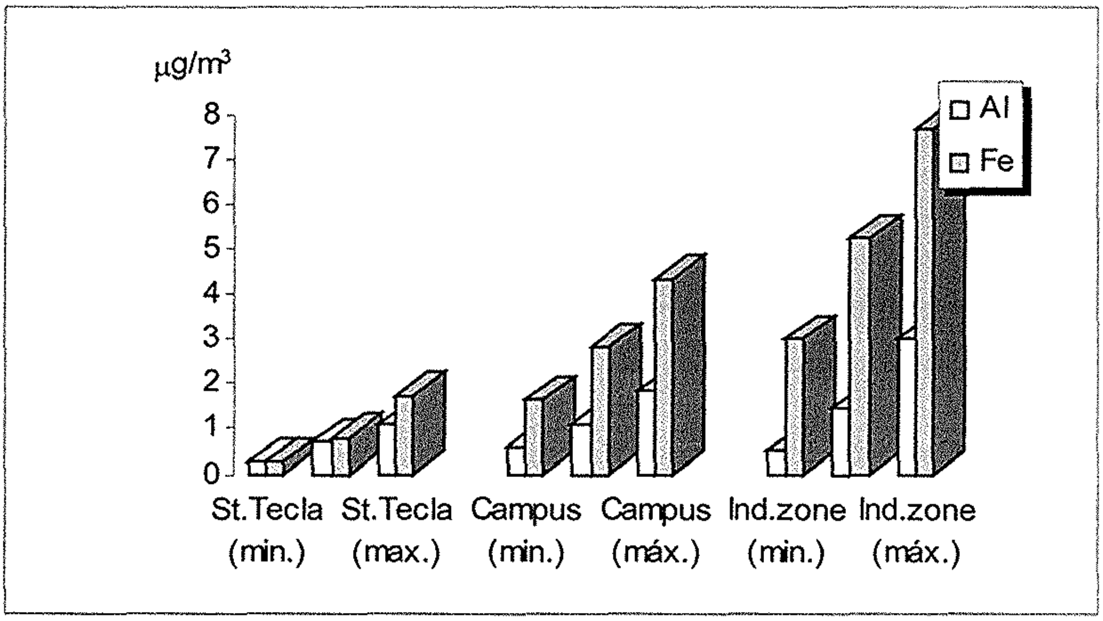

Figure 3. Al and Fe average concentrations in the atmosphere

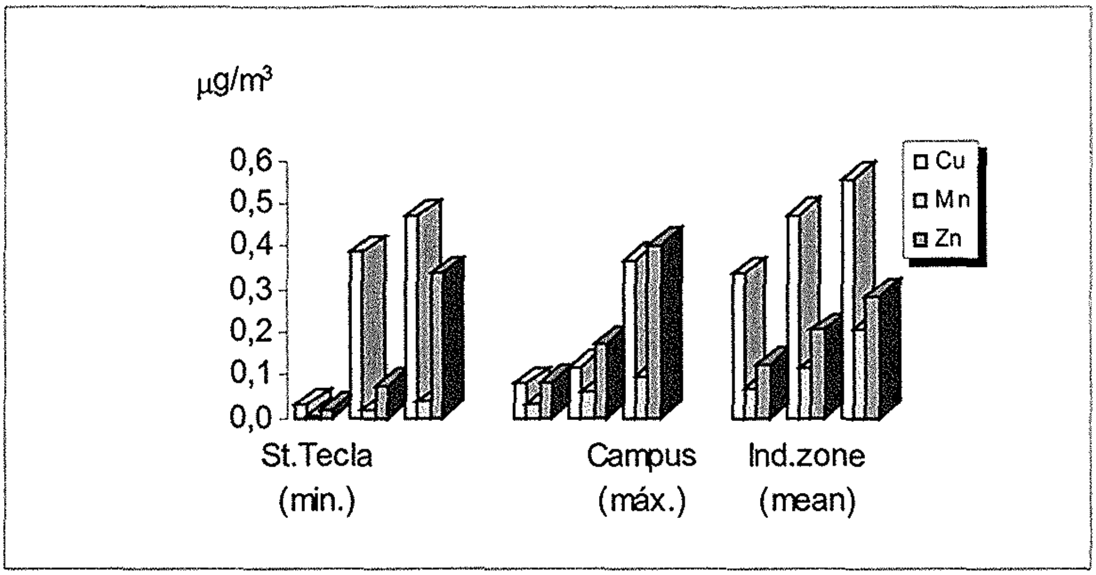

Figure 4. Cu, Mn and Zn average concentrations in the atmosphere

The high concentrations of iron, manganese and zinc, at the intermediary and at the final reaches of the Sapucaia Stream are consequences of the emissions from the industries located in these two zones.

The concentrations of the elements contained in the particles in atmospheric suspension demonstrate a tendency of higher concentrations for the major part of the elements in the industrial region. However, disaggregated particles of uncovered soil areas, agricultural activities and mining around the basin may be considered as great source of aluminum and iron in the atmosphere. The peaks of concentrations for the elements in the urban area (Canoas- Campus) and in the agricultural area (Santa Tecla-Gravataí) are a function of the dispersion of the atmospheric dust.

The significant concentration of copper, in the agricultural area, is caused by its use as fungicidal solution (copper sulfate). Also, this area is near basalt mining activities, a natural source of cooper. Zinc concentrations, in the urban area, are attributed to metal-mechanical and galvanoplasty companies.

The effect of the urban and industrial contamination may be observed by the increase of the concentration of Al, Fe, Cu and Zn (Figures 5,6,7) after point 5 (final reaches area).

These figures also show the filtering action of the wetland area, located at point 2, (where the accumulation of almost all elements is observed) and the reduction of the contamination gradients for water and sediment. At the third point a perceptible reduction of these concentrations occurs, even with the occurrence of sandstone and basalt rocks mining activities in contiguous area, contributing to increase the lixiviated material by rain and wind for the stream´s bed.

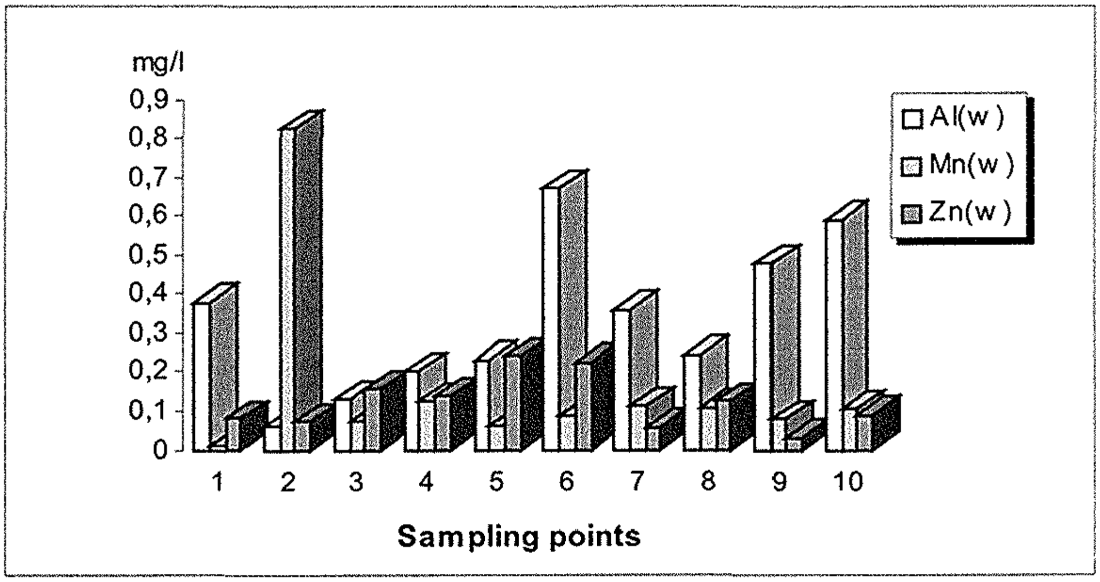

Figure 5. Al, Mn and Zn concentrations in water at different sampling points(winter)

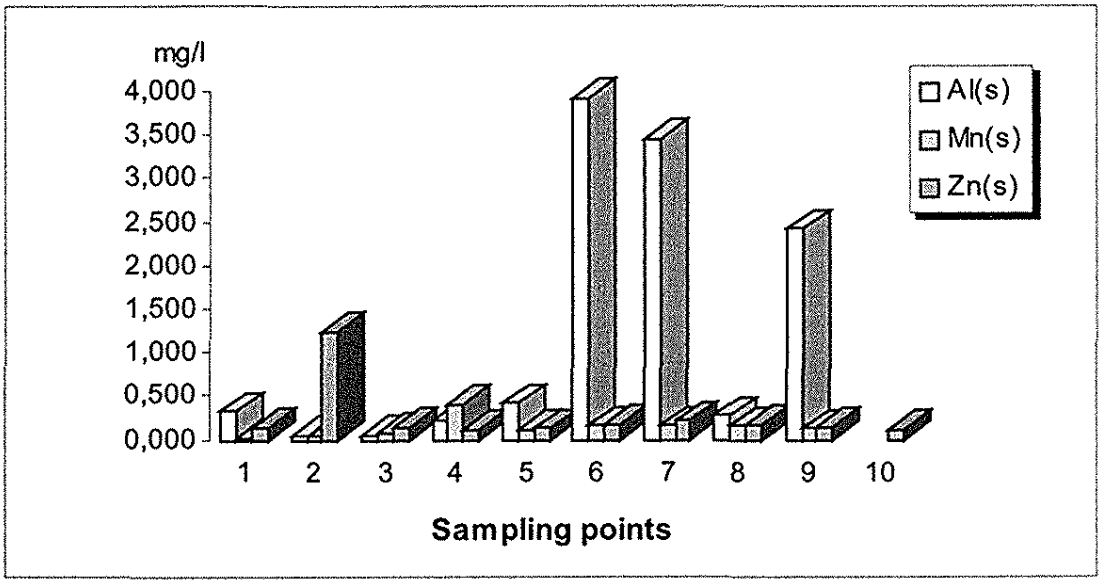

Figure 6. Al, Mn and Zn concentrations in water (summer).

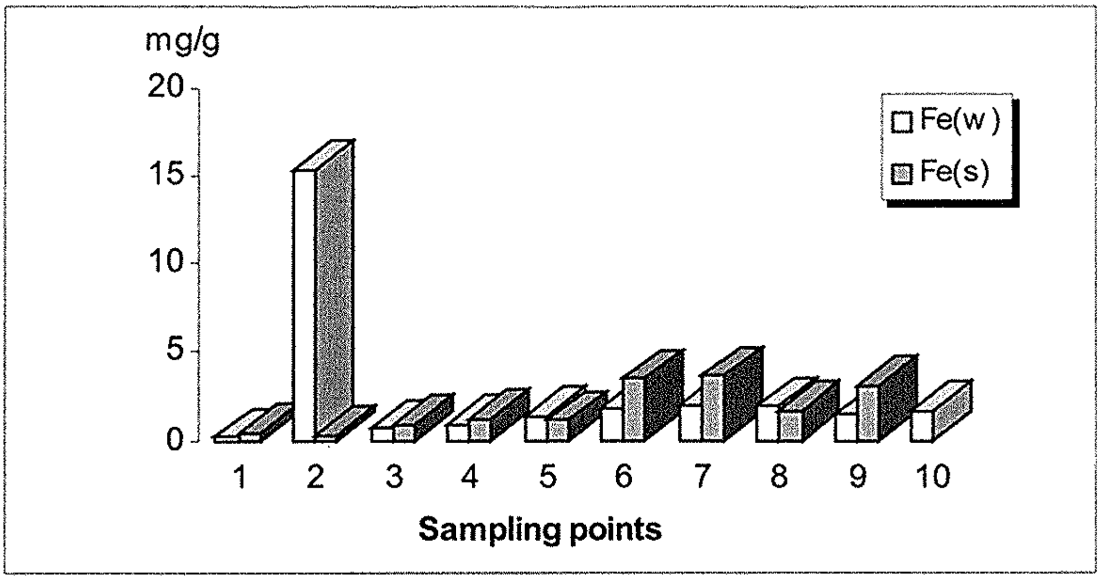

Figure 7. Fe concentrations in water, in winter (w) and summer (s)

High copper concentration in the Santa Tecla region (Figure 8) and at the last sampling points is caused by its use as fungicide. High concentration of copper was also found in the analyzed macrophyte, the *T. diuretica*.

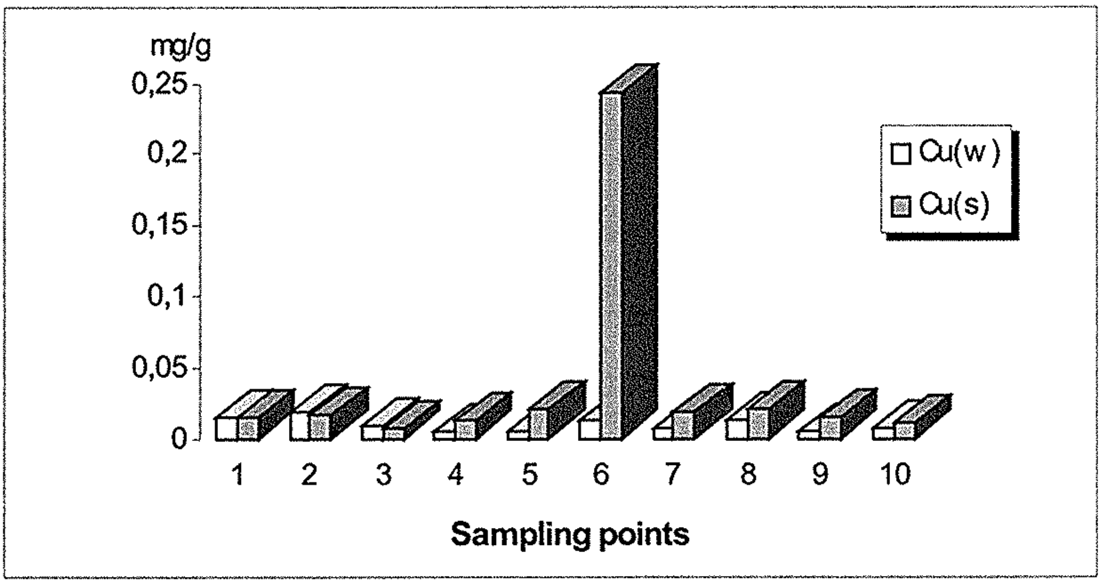

Figure 8. Cu concentrations in water, in winter (w) and summer (s)

During the cold season, an increase in the concentration of iron can be observed in the bathed area. This is probably due to the reduction of the activity of aerobic microorganisms. This leads to the accumulation of organic acids that function as ligands for the iron contained in the sediment and its mobilization for the hydric compartment, due to complexation processes.

Manganese in the hot season presents inverse behavior in relation to the cold season in the wetland area. In the hot season occurs a decrease and in the cold season occurs an increase of its concentration in water. Zinc, with lower concentrations, presents similar behavior to manganese. Copper presented very low concentrations in both seasons. Even so the copper concentrations are higher in the cold season, especially at point 6, near a waste treatment facility in city of Esteio.

A higher aluminium concentration can also be observed at points 6 and 7, probably due to leaching of clays that are the major component of the soils of this region. At point 1, which has higher declivity with regard to point 2, due to the Botucatu Formation[14] sandstone elevations, the concentrations of Al also indicate leaching processes. In the hot season, an increment in the concentrations of this element occurs in the water course.

Figures 9, 10 and 11 present the elements concentrations in the soluble sediments.

The effect of the erosive process on the sandstone and basalt rocks is illustrated by the higher concentrations of Al, Fe and Mn in the upper level reaches of Sapucaia Stream.

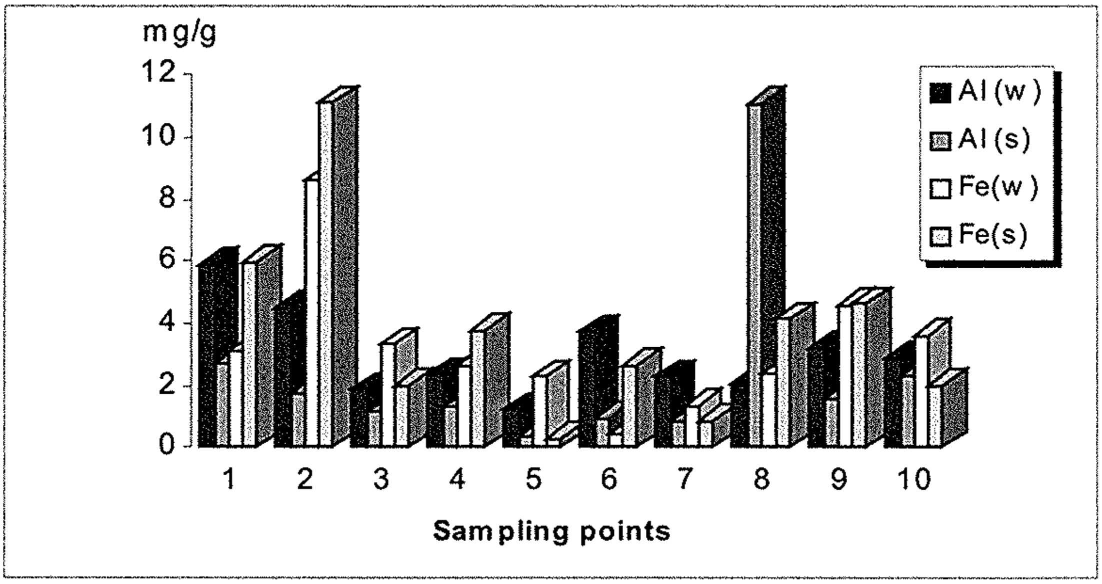

Figure 9. Al and Fe concentrations in sediment (soluble), in winter (w) and summer (s)

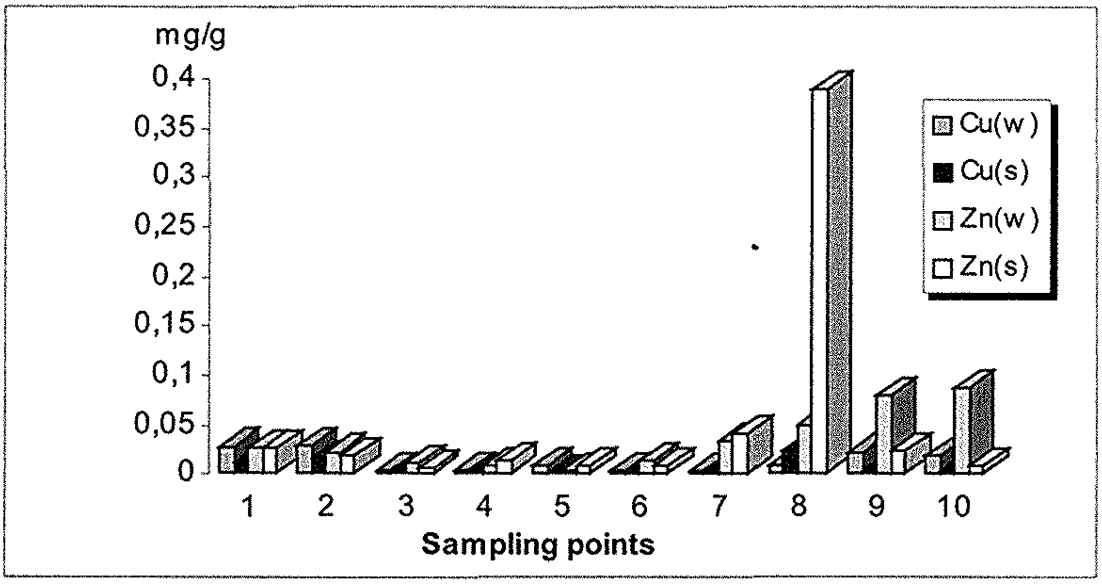

Figure 10. Cu and Zn concentrations in sediment (soluble), in winter (w) and summer (s)

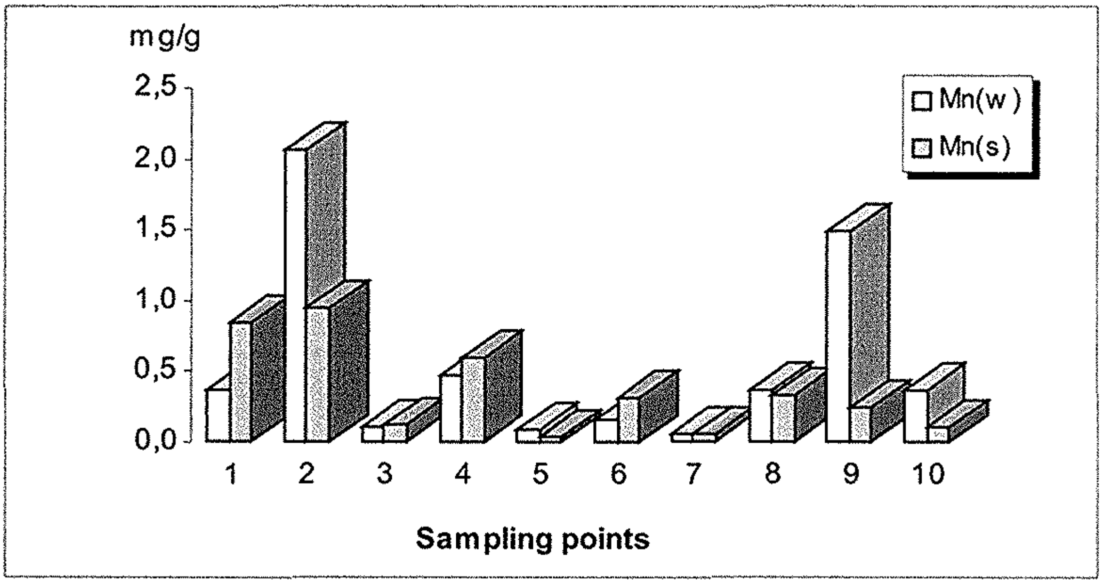

Figure11. Mn concentrations in sidiment (soluble), in winter (w) and summer (s)

It can be seen that the Al, Fe, Zn and Cu concentrations are higger in the final reaches due to the anthropic action.

Figures 12, 13 and 14 present the concentrations of the elements in the macrophytes.

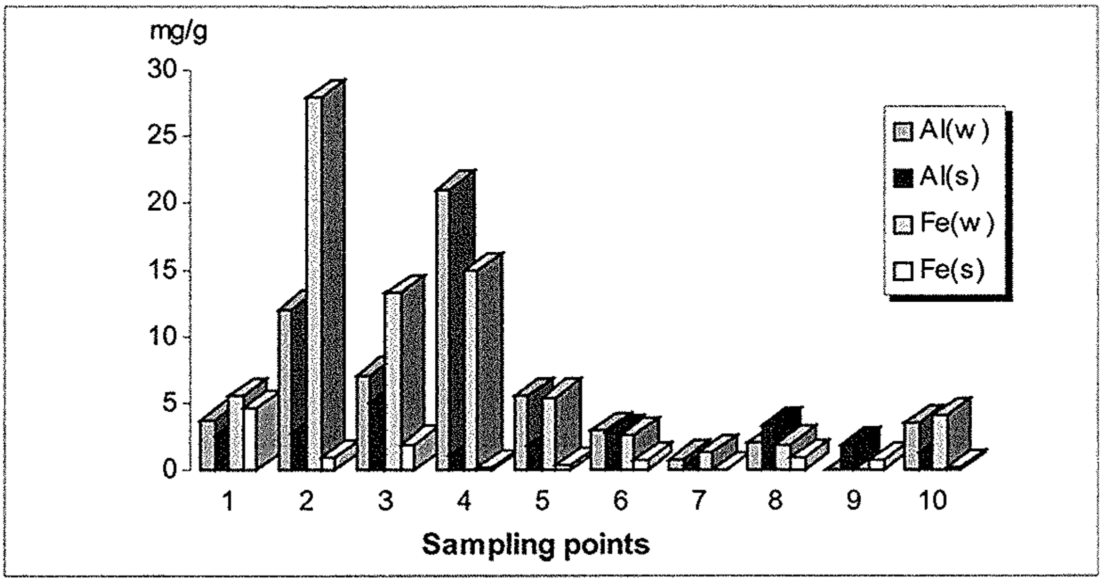

Figure 12. Al and Fe concentrations in macrophytes (mg/g)

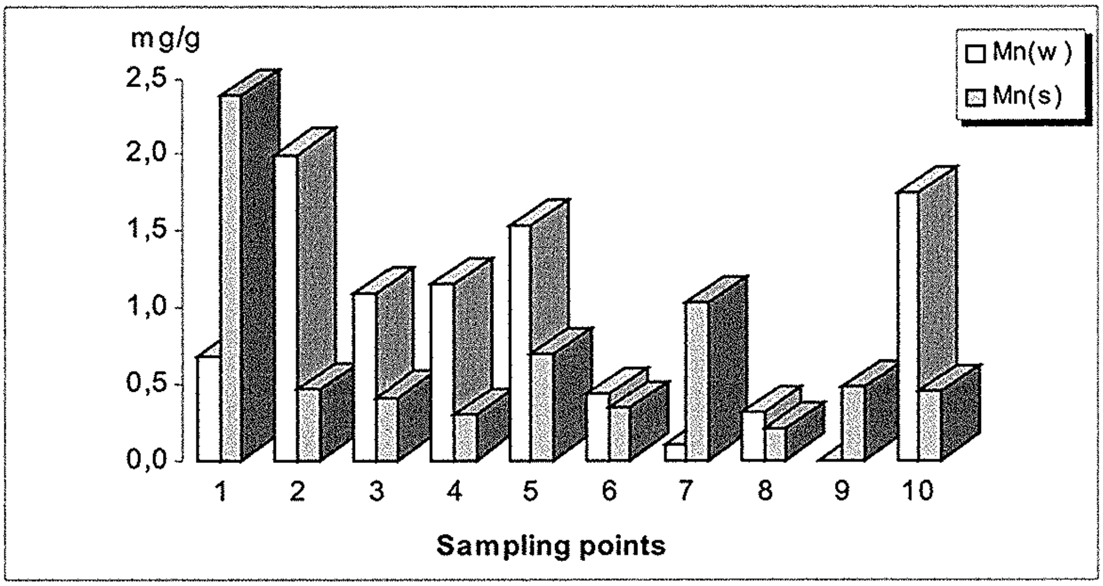

Figure 13. Mn concentrations in macrophytes (mg/g)

The macrophytes present higher Al, Fe and Mn concentrations in the upper reaches. This shows the correlation with the concentrations found in water and in sediments. Also the higher Zn and Cu concentrations in the final reaches show the correlation with the concentrations found in water and in the sediments.

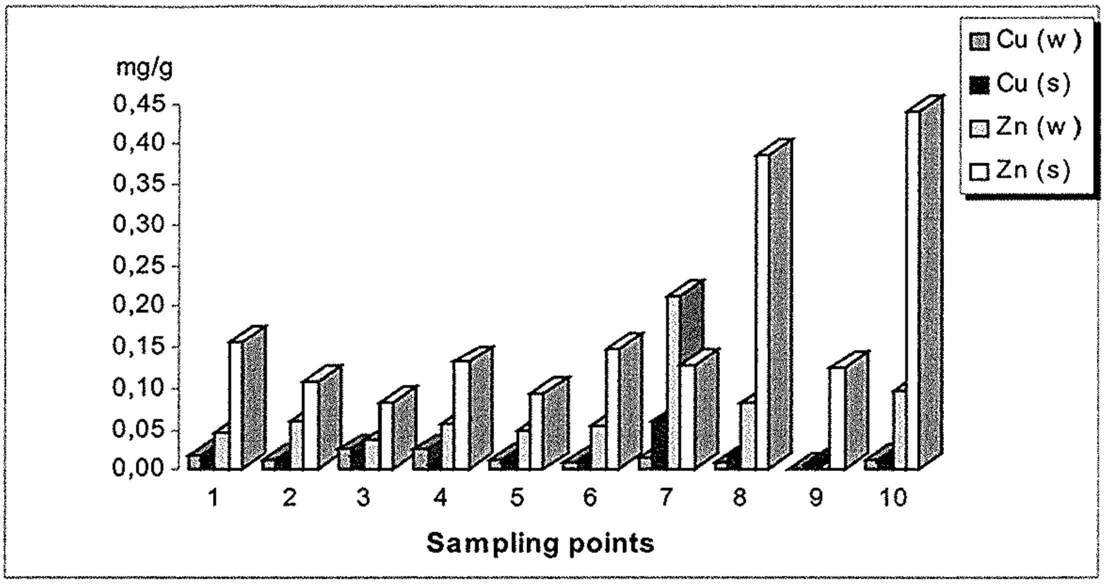

Figure 14. Cu and Zn concentrations in macrophytes (mg/g)

Figure 15 presents the elements concentrations found in fish (*R. quelen*).

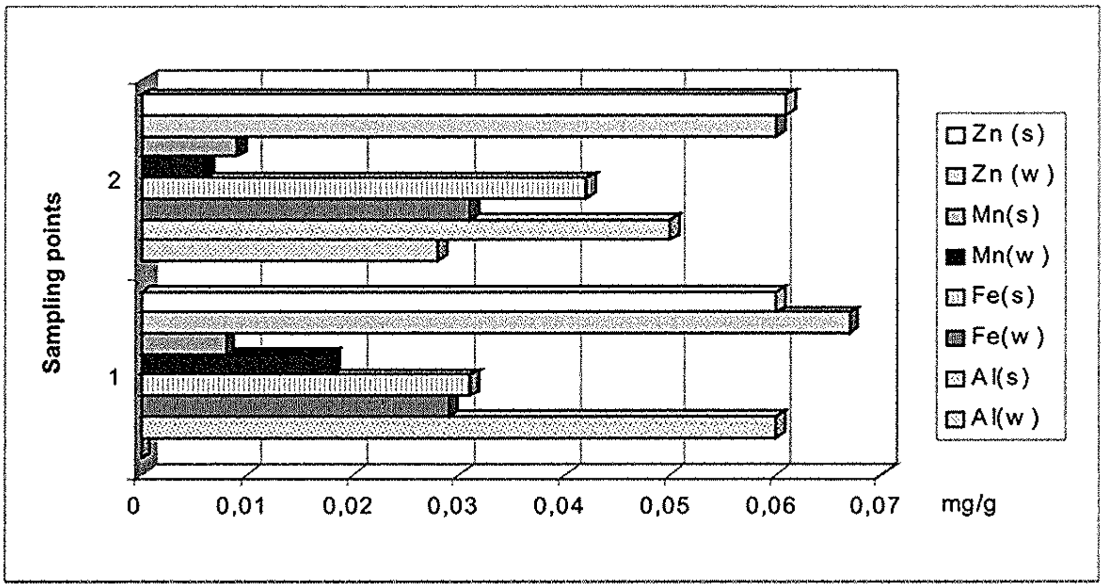

Figure 15. Al, Mn and Zn average concentrations (mg/g) in fish muscle down stream (2) and up stream (1), in winter (w) and summer (s)

It can be observed that, during winter, Zn and Mn have higher concentrations in the upper part of the stream. In the hot season, Fe has a higher concentration in the final reaches and Al in the upper area. Al was detected, by the methods used, only in the final reaches of the urban and industrial area.

The fish collected at sampling points 4 and 8 present no significant differences for lipids peroxidation in the liver. Significantly different average levels of lipids peroxidation were determinated at gills (1.485 nmol TBARS/mg protein, for sampling station 4 and 4.234 nmol TBARS/mg protein, for sampling station 8) and at muscles (0.574 nmol TBARS/mg protein, for sampling station 4 and 4.387 nmol TBARS/mg protein, for sampling station 8) of the collected animals.

CONCLUSIONS

This paper presents the results of the effects of the urban and industrial activities on water and sediment quality of the Sapucaia Stream. At its final course, the great alterations observed in the physico-chemical parameters of water interfere with the water quality of the Sinos River. This river belongs to Guaíba Hydrographic Basin.

At the final reach of the Sapucaia basin, a large increase of metal concentrations in the atmosphere is observed. A correlation was found among the concentrations of some elements in macrophytes, water and soil sediment.

High values for copper were found in the atmosphere and in the macrophyte *T. diuretica* at the upper course. This high concentration of copper may be due to its use in fungicides or mining activities of this region.

Alterations were observed on macrophytes and sediments with the increase of the environment pollution, at the final area of the basin. Significant differences were found for the lipids peroxidation at the gills and at the muscles of the collected fishes in the rural and in the industrial areas.

The water quality of the final area of Sapucaia stream presents alterations which may affect the life quality of the local population.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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CHROMIUM (III) COMPLEX ANIONS IN THE CHEMICAL ANALYSIS. ATROPINE DETERMINATION

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ABSTRACT

Complex anions or Cr(III) analogues of Reinecke's salt, $[Cr(NCS)_2(amine)_2]^-$ are good analytical reagents with high sensibility and selectivity for N-organic bases of pharmaceutical importance. We have observed that the atropine with Cr(III) complex anions. Some new oxidative methods for determination of atropine are described. The results were evaluated statistically.

KEYWORDS: chromium (III), atropine, drugs, oxidimetric and spectrometric methods.

RESUMO

Complexos aniónicos de Cr(III), análogos do sal de Reinecke, são reagentes analíticos excelentes a possuem sensibilidade e seletividade alta para para bases orgánicas de N que tem importancia farmacéutica. O presente estudo demonstrou que a atropina forma precipitados com aniones complexos de Cr(III). Os resultados experimentáis foram avaliados estatisticamente.

INTRODUCTION

Atropine is the ester of the tropic acid with tropanol. This alkaloide is found along with other compounds with similar structure in the leaves, the seeds and the roots of some plants from *Solanaceae* family: "*Atropa belladona,Datura stramonium* and *Hyoscyamus niger*".

Atropine is racemic form and always accompanies hiosciamine which is its levogyre isomer.

It has been proved that the atropine is formed by the partial racemization of the hiosciamine during the drying of these vegetal products as well as during the isolation of the alkaloide, but it has been found as such in the plants mentioned above.

For the industrial extraction of this alkaloide the dry or fresh vegetal material, is impregnated with a 10% Na_2CO_3 solution and then is put into an extraction apparatus where is used up with ether. After removing the ether, the solution lets an oily liquid.

By adding 5% acetic acid, the alkaloides in the oily liquid are transformed in acetates, which are held in a cold place for 24 hours. Then, they are filtered, are neutralized with ammonium hydroxide and they are alkalinized with potassium carbonate till the appearance of an opalescence.

From this solution, the crude alkaloide precipitates in a crystalline form which is filtered, washed with distilled water and is dried in air [1].

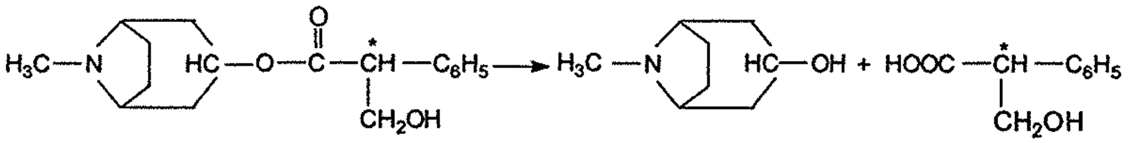
The crude product is dissolved in ether in order to be purified and animal coal is added for discolouring. The ether can be replaced with other solvents like a mixture of benzene and gazoline.

The pure product obtained after moving off the solvent at 120 °C during a few hours, is filtered, is washed with acetone and is dried in the open air.

The structure formulae of this alkaloide was established through degradation reactions (hydrolysis, oxidation, etc.).

Willstätter's works contain a complete study about the structure of this alkaloide.

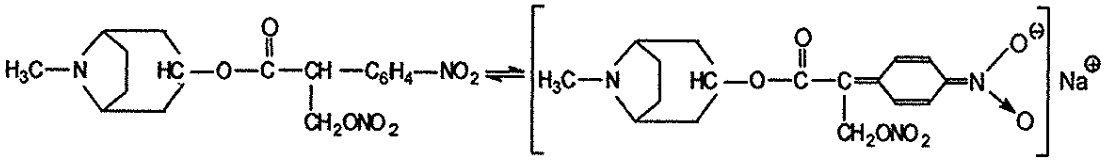
Atropine is hydrolyzsed in tropanol and tropic acid under the action of concentrated HCl and $Ba(OH)_2$ as follows:


atropine tropanol tropic acid

The atropine is a base which forms crystalline salts with the mineral acids. It precipitates with picric acid and forms an yellow picrate with 175 °C melting point; with $H_2[PtCl_6]$ the atropine forms an yellow precipitate with a melting point of 207 °C and with $H[AuCl_4]$ also forms an yellow precipitate but with a melting point of 136 °C etc.

Two colour reactions are used for the identification of the atropine, for example:

- Vitali's reaction, which is a nitration reaction of tropic acid with the formulae:

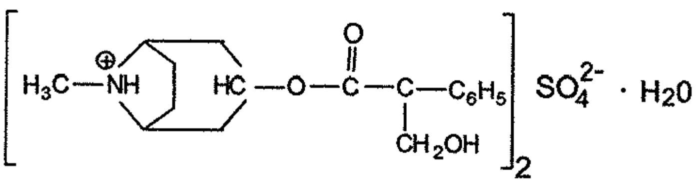


- Wasicky's reaction with p-dimethyl-aminobenzaldehyde in H_2SO_4 when a red-violet colour is obtained.

The atropine sulphate is more used in therapy then the valerianate. The atropine sulphate is a crystalline chemical compound, without aroma, and with bitter sour taste.

It is melted at 195°C and is soluble in water and alcohol in 1:1 molar raport, insoluble in ether, chloroform and benzene. The aqua solution has a neutral reaction.

The structural formulae of the sulphate atropine is as follows:



Vitali's reaction is used for the identification of the alkaloide and the reaction with $BaCl_2$ is used for the sulphate anion.

The quantitative determination of the sulphate atropine is done acido-basic in non aqua medium with 0.1 N perchloric acid in acetic acid using as titration medium a mixture of acetic acid and acetic anhydride and as indicator alpha naphtol benzeine when a green colour is obtained.

The atropine has parasympatholytic action: it relaxes the muscles of the gastro-intestinal and genito-urinary tract, and the biliary muscles. The atropine is used in ophthalmology and because of its pain-killer action is utilized as ointment for neuralgia and for hemorrhoidal pain. The atropine is preserved in airtight bottles.

EXPERIMENTAL PROCEDURE. RESULTS AND DISCUSSIONS

The synthesis of the complex salts of the type Atropine·H[Cr(NCS)$_4$(ammine)$_2$]

20 Mmoles atropine sulphate are acidulated with 10 mL of 1 N H_2SO_4 and then 80-100 mL distilled water are added.

The atropine sulphate is precipitated with 10 Mmoles reagent of the type tetratiocianatochromat (III) which is dissolved in 15 mL ethanol. A crystalline precipitate with a red-violet colour is formed and after 10-15 minutes it is filtered under vacuum [2,3,4].

The precipitate is washed with distilled water till the filtrate becomes colorless and then it is laid down at air to dry

The experimental results are presented in table 1.

Table 1. New complex salts of the type Atropine·H[Cr(NCS)$_4$(ammine)$_2$]

No.	The combination	Molecular weight calcd.	Yield %	Solubility mol/L	Microcrystalline aspect	Analysis %	
						Calcd.	Found
1	AH[Cr(NCS)$_4$(NH$_3$)$_2$]	588,75	91	$3 \cdot 10^{-2}$	Violet-red microcrystales	Cr:8,83 S:21,78 N:16,64	8,77 21,66 16,55
2	AH[Cr(NCS)$_4$(aniline)$_2$]	760,88	98	$1{,}8 \cdot 10^{-2}$	Violet-red microcrystales	Cr:6,83 S:16,85 N:12,87	6,80 16,70 12,69
3	AH[Cr(NCS)$_4$(benzilamine)$_2$]	788,88	96	$1{,}9 \cdot 10^{-2}$	Violet-red microcrystales	Cr:6,59 S:16,25 N:12,42	6,48 16,16 12,33
4	AH[Cr(NCS)$_4$(imidazole)$_2$]	711,04	88	$6 \cdot 10^{-2}$	Violet-red microcrystales	Cr:7,31 S:18,03 N:17,72	7,29 17,88 17,57
5	AH[Cr(NCS)$_4$(benztriazole)$_2$]	813,92	94	$2{,}5 \cdot 10^{-2}$	Violet-red microcrystales	Cr:6,39 S:15,75 N:18,92	6,27 15,70 18,88
6	AH[Cr(NCS)$_4$(urotropine)$_2$]	855,02	93	$4 \cdot 10^{-2}$	Violet-red microcrystales	Cr:6,08 S:14,99 N:21,28	6,03 14,93 21,24

A = atropine

Chromium was determinated as Cr_2O_3; sulphur was determinated as $BaSO_4$; nitrogen was determinated by combustion.

Gravimetric determination of atropine as Atropine·H[Cr(NCS)$_4$(NH$_3$)$_2$] (A) and Atropine·H[Cr(NCS)$_4$(aniline)$_2$] (B)

A sample of 1.67 – 16.7 mg atropine is acidulated with 5 mL 0,1 HCl and then it is precipitated with the analytical reagent into a 3% alcohol – water solution.

The obtained precipitate is filtered with a G_4 crucible, is washed 3-4 times with 10 mL 3% alcohol – water solution till the filtrate flows colourless. The precipitate is dried one hour at 105 °C into an oven [5,6].

The experimental results are presented in table 2.

Table 2. Gravimetric determination of atropine as Atropine·H[Cr(NCS)$_4$(NH$_3$)$_2$] (A) and Atropine·H[Cr(NCS)$_4$(aniline)$_2$] (B)

No.	Atropine taken mg	The form of determination							
		A				B			
		$G_{complex}$ found mg	Atropine found mg	Error		$G_{complex}$ found mg	Atropine found mg	Error	
				mg	%			mg	%
1	1.67	3.38	1.66	-0.01	0.60	4.37	1.66	-0.01	0.59
2	3.34	6.78	3.33	-0.01	0.29	8.76	3.33	-0.01	0.30
3	6.68	13.56	6.66	-0.02	0.29	17.63	6.70	+0.02	0.30
4	10.02	20.37	10.01	-0.01	0.09	26.31	10.00	-0.02	0.20
5	13.36	27.23	13.38	+0.02	0.15	35.17	13.37	+0.01	0.07
6	16.70	33.97	16.69	-0.01	0.18	43.88	16.68	-0.02	0.12
		$M_A = 588.75$; $f_A = 0.4914$; $\overline{X} = 10.03$; $S^2 = 6.33 \cdot 10^{-4}$; $S = 2.52 \cdot 10^{-2}$; $t = 0.40$; $t_{n-1,\alpha} = 2.37$; $\alpha = 95$ %; $\overline{X} - t \cdot S < A < \overline{X} + t \cdot S$; $10.01 < 10.02 < 10.04$				$M_B = 760.88$; $f_B = 0.3802$; $\overline{X} = 13.37$; $S^2 = 5 \cdot 10^{-4}$; $S = 2.23 \cdot 10^{-2}$; $t = 0.45$; $t_{n-1,\alpha} = 2.37$; $\alpha = 95$ %; $\overline{X} - t \cdot S < A < \overline{X} + t \cdot S$; $13.35 < 13.36 < 13.38$			

The oxidimetric determination of atropine after precipitation as Atropine·H[Cr(NCS)$_4$(NH$_3$)$_2$](A), Atropine·H[Cr(NCS)$_4$(aniline)$_2$] (B) respectively

1.67 – 13.36 mg atropine are acidulated with 5 mL 0,1 M HCl then, the mentioned analytical reagent is added in water or 3% alcohol – water solution, when red-violet precipitates are formed. These precipitates are filtered and washed with distilled water till the filtrate flows colourless. The paper with the precipitate is brought into a 500 mL Berzelius glass together with 20 mL 5% NaOH in order to decompose and to liberate NCS$^-$ anion.

Each sample is acidulated with HCl till the normal concentration becomes 1.7-2 N. The quantity of HCl is calculated using the relation:

$$V_{HCl} = \frac{1.7\left(V_{initial} + V_{oxidizer}\right)}{10.4}$$

An amount of 5 mL $CCl_4$and 10 drops of ICl indicator solution[7] are added in the Berzelius glass and NCS^- free is titrated with 0.1 N $KMnO_4$, $KBrO_3$ or KIO_3 solution under stirring. When the no watery stratum is discoloured the end of the titration may be considered

The advantage of this titration is the favorable stoechiometry, because one equivalent of NCS^- consumes six equivalents of oxidizer ($KMnO_4$, $KBrO_3$ or KIO_3).

The reactions which take place are:

$$5\ NCS^- + 6\ MnO_4^- + 13\ H^+ \rightarrow 6\ Mn^{2+} + 5\ SO_4^{2-} + 5\ HCN + 4\ H_2O$$

Respectively:

$$2\ NCS^- + 3\ BrO_3^- + 4\ H^+ \rightarrow 2\ SO_4^{2-} + 3\ Br^+ + 2\ HCN + H_2O$$
$$2\ NCS^- + 3\ IO_3^- + 4\ H^+ \rightarrow 2\ SO_4^{2-} + 3\ I^+ + 2\ HCN + H_2O$$

The experimental results are presented in table 3:

Table 3. The oxidimetric determination of atropine after precipitation as Atropine·$H[Cr(NCS)_4(NH_3)_2]$, Atropine·$H[Cr(NCS)_4(aniline)_2]$ (B) respectively

Atropine taken mg	No. det.	Average of determinations $\overline{X}$ (mg)	Square average Error adequate one determination (S)	t_a	t_b	$t_{n-1,\alpha}$ α =95 %
Permanganometric determination						
1.67	10	1.682	$2.66\cdot10^{-2}$	$4.7\cdot10^{-4}$	$5.13\cdot10^{-2}$	2.57
6.68	10	6.687	$2.77\cdot10^{-2}$	$0.28\cdot10^{-4}$	$5.05\cdot10^{-2}$	2.57
Bromatometric determination						
3.34	10	3.332	$1.94\cdot10^{-2}$	$3.06\cdot10^{-4}$	$5.03\cdot10^{-2}$	2.57
10.02	10	10.029	$2.52\cdot10^{-2}$	$9.12\cdot10^{-4}$	$4.98\cdot10^{-2}$	2.57
Iodatometric determination						
6.68	10	6.673	$2.23\cdot10^{-2}$	$26.66\cdot10^{-4}$	$5.31\cdot10^{-2}$	2.57
13.36	10	13.373	$2.23\cdot10^{-2}$	$21.89\cdot10^{-4}$	$4.83\cdot10^{-2}$	2.57

Spectrometric determination of atropine with complexes anions of Cr (III)

Amounts of 2.28 – 18.24 mg atropine are acidulated with 5 mL 0.1 M HCl, are completed till 50 mL with a 3% alcohol – water solution and is added ammonium rhodanilat $H_4N[Cr(NCS)_4(aniline)_2]$.

The obtained red-violet precipitate is filtered using a G_4 porosity glass filter, is washed 3 or 4 times with 10 mL alcohol-water (1:1) and then is dissolved in acetone. The obtained solution is brought into a 25 mL balloon and acetone is added till the sign. The absorbance is determinated at 540 nm.

The experimental data were statistically interpreted through the linear regression method and they are presented in table 4:

Table 4. Spectrometric determination of atropine as Atropine·H[Cr(NCS)$_4$(aniline)$_2$]

No.	X (mg)	X^2	Y	Y^2	X·Y	X+Y	$(X+Y)^2$
1	2.28	5.1984	0.04	0.0016	0.0912	2.32	5.3824
2	4.56	20.7936	0.08	0.0064	0.3648	4.64	21.5296
3	6.84	46.7856	0.11	0.0121	0.7524	6.95	48.3025
4	9.12	83.1744	0.15	0.0225	1.3680	9.27	85.9329
5	11.40	129.9600	0.19	0.0361	2.1660	11.59	134.3281
6	13.68	187.1424	0.23	0.0529	3.1464	13.91	193.4881
7	15.96	254.7216	0.27	0.0729	4.3092	16.23	263.4129
8	18.24	332.6976	0.31	0.0961	5.6544	18.55	344.1025
Total	82.08	1060.4736	1.38	0.3006	17.8524	83.46	1096.479

Using the data presented in table 4 we can do the next calculations:

$$\sum X^2 + \sum Y^2 + 2\sum X \cdot Y = 1096.479$$
$$\sum (X+Y)^2 = 1096.479$$

It is observed that both values are equal. This means that the method elaborated by us is reproducible and accurate.

The standard deviations and the regress coefficient are calculated thus:

$$\sigma_X = \sqrt{\frac{\sum X^2}{n} - \overline{X}^2} = 5.224; \quad \overline{X} = 10.26$$
$$\sigma_Y = \sqrt{\frac{\sum Y^2}{n} - \overline{Y}^2} = 0.0884; \quad \overline{Y} = 0.1725$$
$$r = \frac{\frac{\sum XY}{n} - \overline{X} \cdot \overline{Y}}{\sigma_X \cdot \sigma_Y} = 0.9998 \cong 1$$

The value of r shows that the results obtained by this method are reproducible and the error is negligible.

The equations infered through the method of linear regression, which show in the best way the dependence between the absorbance and the concentration of the active product in the sample (mg) are the following:

$$Y - \overline{Y} = r \cdot \frac{\sigma_Y}{\sigma_X}\left(X - \overline{X}\right); \quad Y = 0.0169185 \cdot X - 0.00108395$$
$$X - \overline{X} = r \cdot \frac{\sigma_X}{\sigma_Y}\left(Y - \overline{Y}\right); \quad X = 59.0832036 \cdot Y + 0.06814737$$

The domain of concentrations in which the Lambert – Beer law is valid is contained between 0.0912 and 0.7296 mg atropine.

The molar coefficient of absorbance is $\varepsilon = 323.29\ \mathrm{l \cdot cm^{-1} \cdot mol^{-1}}$.

The calibration curve for the spectrometric determination of atropine as Atropine·H[Cr(NCS)$_4$(aniline)$_2$] is presented in the figure 1.

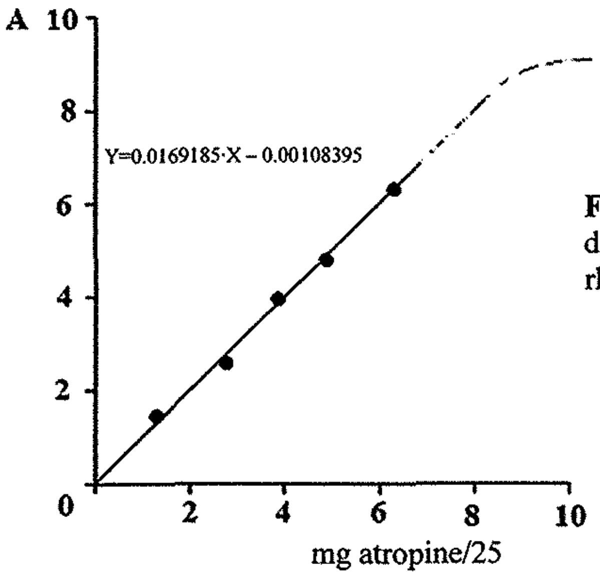


Fig.1. The calibration curve for the determination of atropine with ammonium rhodanilat.

CONCLUSIONS

New methods of determination of atropine as Atropine·$H[Cr(NCS)_4(aniline)_2]$ were elaborated.

All the experimental results were statistically analysed and it came out that the methods elaborated by us are not affected by systematic errors, are rapid, accurate enough, so that we recommend these methods to be used in the laboratories of control and analyses of drugs.

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SYNTHESIS OF NANOCRYSTALLINE NICKEL OXIDE POWDERS VIA GLYCINE-NITRATE COMBUSTION

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ABSTRACT

NiO is a candidate material for a variety of potential applications, for example, active optical filters, antiferromagnetic layers, coloring agents for enamel, pigments, catalysts, cathode materials for alkaline batteries and temperature sensors. Nanocrystalline nickel oxide powders have been synthesized by the combustion technique using glycine as a fuel and nitrate as an oxidizer. The precursor solution was heated to evaporate water, yielding a viscous liquid. It ignited and underwent self-sustaining combustion, producing an ash composed of the oxide product. The as-synthesized particles have been characterized by X-ray diffraction (XRD), and scanning electron microscopy (SEM). Nanocrystalline nickel oxide was possible to be obtained from fuel-lean ratios. The smallest crystallite size was obtained under fuel-lean (0.09) formulation. The size of the NiO nanoparticles varied from 4 to 18 nm.

KEYWORDS: Ceramics; Nanoparticle chemical synthesis; X-ray diffraction; Thermodynamic properties.

RESUMO

O NiO é um material candidato para uma variedade de aplicações: filtros óticos ativos, camadas antiferromagnéticas, agentes corantes para vidrados, pigmentos, catalisadores, cátodos como materiais para baterias alcalinas e sensores de temperatura. Pós de óxido de níquel nanocristalino foram sintetizados pela técnica de combustão, usando glicina como combustível e nitrato como oxidante. A solução precursora foi aquecida até evaporar a água, gerando um líquido viscoso. Ela sofre ignição e combustão auto-sustentada, produzindo uma cinza a qual é composta de um óxido como produto. As partículas como-sintetizadas foram caracterizadas pela difração de raios X (DRX), e microscopia eletrônica de varredura (MEV). O óxido de níquel nanocristalino foi obtido de reações deficientes em combustível. O menor tamanho de cristalito foi obtido com a formulação deficiente em combustível (0.09).Os tamanhos de nanopartículas de NiO variaram de 4 a 18 nm.

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INTRODUCTION

Nanoscale oxide particles are gaining increasing technical importance for classic areas of application such as catalysts, passive electronic components, and ceramic materials[1]. NiO nanoparticles are desirable for many applications in the manufacture of ceramic, magnetic, electrochromic and heterogeneous catalytic materials.

The technique of combustion synthesis is an inexpensive method to produce oxides and mixtures of submicrometric or nanometric powders. This method consists of heating an aqueous solution made of inorganic salts, usually nitrates which act as an oxidant agent and an organic combustible, which can be also a complexant agent of the metallic ions. Firstly, it is necessary to ensure the homogeneity of the system with the complete dissolution of the components. After that, the solution is heated until its ignition, giving rise to a fast exothermic reaction that leads to oxides formation. The complexant/combustible agent plays a fundamental function preventing the precipitation of the individual precursors prior the ignition.

In this article, we described experiments employed to synthesize NiO powders by different fuel-to-oxidant molar ratios using glycine as complexant/combustible agent and nitrate as an oxidizer. The produced powder was characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) Enthalpies and adiabatic flame temperatures can be calculated for the different formulations.

EXPERIMENTAL

Nickel nitrate $Ni(NO_3)_2.6H_2O$ (Vetec Química, Brazil) and glycine (Synth, Brazil) with 97% and 98.5% purities respectively (vendor specification) were used as the starting material. These salts were dissolved in 80 mL of water in the appropriate amount to obtain the desired molar proportion.

The ignition of the solution containing a complexant/combustible agent and the precursor salts was carried out in an electrical oven at 400°C. A 500ml stainless steel recipient was used to perform the ignition process. A portion of the solution was reserved to TGA/DTA analysis. The general flowchart for the process is shown in Fig. 1.

Before the combustion, small portions of each mixture were separated for thermal gravimetric (TG) and differential thermal analyses (DTA) according to the Boersma method[2]. A STA Harrop 736 thermal analyzer was used. Platinum crucibles containing 34±4mg of material were used; they were heated up to 800°C at a rate of 10K/min and 50 mL/min air gas flow. XSEM micrographs were recorded with a Jeol (model JSM-5800) instrument after coating the samples with gold.

All the samples were analyzed with a Philips (model X'Pert MPD) diffractometer, equipped with a graphite monochromator and a rotative anode of copper operating a 40 kV and 40 mA. All measurements were made using Cu Kα radiation; the scanning rate was 1°/min for phase analysis and 0.4°/min for crystallite size determination.

WinFit 1.0 software was used to determine the crystallite size of the synthesized powders. The profile shape function used was a split Pearson VII function and the single line variance approach of Toth[3] and Arkai and Toth[4] was considered for the crystallite size calculation. The $K_{\alpha 2}$ contribution was removed by the Rachinger correction, and the Stokes deconvolution method was employed to remove the instrumental contribution of the experimental peaks after introducing the profile shape function of pure-line standard. A sample of nickel oxide, which was annealed at 1000 °C for 4 h, was used as standard. Very sharp and well defined peaks were obtained with this procedure. From the Pearson exponent of the profile shape function, the contribution of Gaussian and Lorentzian components could be calculated. Such contributions are assumed to be proportional to the amount of crystallite size broadening and strain broadening, respectively. Finally, Fourier analysis was used to calculate size and strain parameters.

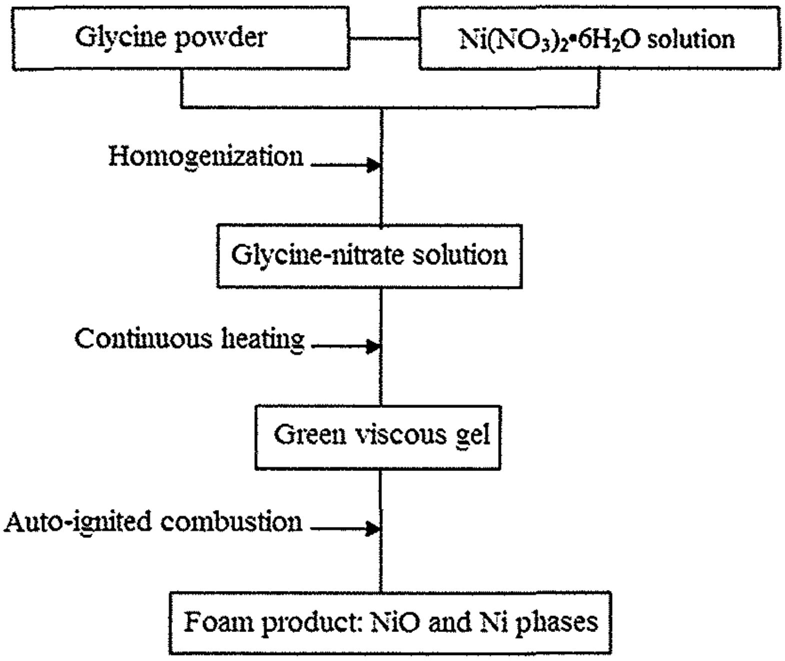


Fig. 1. Flowchart of the synthesis process.

RESULTS AND DISCUSSION

A typical DTA run of the mixture is shown in Fig. 2. This precursor solution dehydrates endothermically, with broad peak at 80-150 °C. The small exothermic peak around 215 °C is attributed to the rapid combustion wave front which burns all existing organic phases. From the TG graph it is also observed that the precursor solution exhibited a tumble loss weight up to 25 °C due to dehydration. It is also verified a second drop around 215 due to the organic matter loss. Actually, the ignition temperature does not depend on the fuel-to-oxidant ratio in accordance with evaluated experiments.

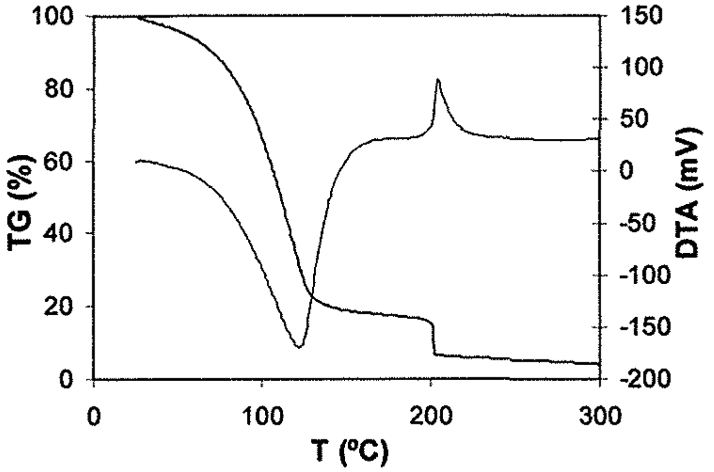


Fig. 2. Simultaneous TG-DTA curves of the precursor glycine-to-nitrate solution.

Thermodynamic considerations

The combustion of nickel nitrate-glycine mixture appears to undergo a self-propagating and non-explosive exothermic reaction.

A stoichiometric mixture of fuel and oxidant is one in which the quantity of oxidant present is theoretically correct for complete oxidation[5]. The reaction occurs in the presence of air. Any thermodynamic calculation involving flame temperature must also take into account the oxygen and nitrogen present in air.

The first reaction illustrated bellow gives the true stoichiometric reaction. The fuel-rich reactions involve increase in glycine with respect to the stoichiometric equation. On the other hand, the fuel-lean reactions involve a decrease in the quantity of glycine. In both cases the amount of nitrate is maintained constant. All experimental combustion reactions were carried out in the presence of air.

Stoichiometry (0.37) (S)

$$1.0\ Ni(NO_3)_2.6H_2O + 1.11\ NH_2CH_2COOH \rightarrow 1.0\ NiO + 1{,}55\ N_2 + 2.22\ CO_2 + 8.77\ H_2O$$

(Eq. 1)

Fuel-rich (+ 50%, 1.11) (**R1**)

$$1.0\ Ni(NO_3)_2.6H_2O + 1.66\ NH_2CH_2COOH + 1.23\ O_2 \rightarrow 1.0\ NiO + 1.83\ N_2 + 3.32\ CO_2 + 10.15\ H_2O$$

(Eq. 2)

Fuel-rich (+ 100%, 0.55) (**R2**)

$$1.0\ Ni(NO_3)_2.6H_2O + 2.22\ NH_2CH_2COOH + 2.49\ O_2 \rightarrow 1.0\ NiO + 2.11\ N_2 + 4.44\ CO_2 + 11.55\ H_2O$$

(Eq. 3)

Fuel-rich (+ 200%, 0.74) (**R3**)

$$1.0\ Ni(NO_3)_2.6H_2O + 3.33\ NH_2CH_2COOH + 4.99\ O_2 \rightarrow 1.0\ NiO + 2.66\ N_2 + 6.66\ CO_2 + 14.32\ H_2O$$

(Eq. 4)

Fuel-lean (- 25%, 0.24) (**L1**)

$$1.0\,Ni(NO_3)_2.6H_2O + 0.72\,NH_2CH_2COOH \rightarrow 1.0\,NiO + 1.36\,N_2 + 1.44\,CO_2 + 0.88\,O_2 + \\ + 7.8\,H_2O$$

(Eq. 5)

Fuel-lean (- 50%, 0.18) (**L2**)

$$1.0\,Ni(NO_3)_2.6H_2O + 0.55\,NH_2CH_2COOH + \rightarrow 1.0\,NiO + 1.28\,N_2 + 1.1\,CO_2 + 1.26\,O_2 + \\ + 7.38\,H_2O$$

(Eq. 6)

Fuel-lean (- 75%, 0.09) (**L3**)

$$1.0\,Ni(NO_3)_2.6H_2O + 0.28\,NH_2CH_2COOH + \rightarrow 1.0\,NiO + 1.14\,N_2 + 0.56\,CO_2 + 1.87\,O_2 + \\ + 6.7\,H_2O$$

(Eq. 7)

Available thermodynamic data in literature[6,7] for various reactants and products are presented in Table 1. It is well known that the enthalpy of combustion can be expressed as:

$$\Delta H^0 = \left(\sum n\Delta H_p^0\right) - \left(\sum n\Delta H_r^0\right)$$

and

$$\Delta H^0 = \int_{T_0}^{T} \left(\sum nC_p\right) dT \ , \quad \text{or} \quad T = T_0 + \frac{\Delta H_r^0 - \Delta H_p^0}{C_p}$$

where n is the number of the mol, ΔH_r^0 and ΔH_p^0 are the enthalpies of formation of the reactants and products, respectively, T is the adiabatic flame temperature, T_0 is 298 K and Cp is the heat capacity of products at constant pressure. Using the thermodynamic data for various reactants and products listed in the Table 1, the enthalpy of combustion and the theoretical adiabatic flame temperatures as a function of glycine-to-nitrate molar ratio can be calculated. Nevertheless, the measured flame temperatures are typically much lower than calculated values as a result of radiative losses, incomplete combustion, and heating of air.

The adiabatic flame temperature T of the reaction is influenced by the type of fuel, fuel to oxidizer ratio, and the amount of water remaining in the precursor solution at the ignition temperature[8]. The [illegible] temperature can be increased with the addition of excess oxidizer such as ammonium nitrate[9], or by increasing the fuel/oxidizer molar ratio. Segadães et al.[10] calculated theoretical adiabatic flame temperatures in the case of urea–nitrate combustion synthesis of ZnO. Purohit et al.[5] also calculated theoretical adiabatic flame temperatures involving glycine-nitrate combustion synthesis of CeO_2.

The variation of enthalpy with the glycine-to-nitrate molar ratio could be seen in Fig. 3. As expected, they increase substantially with the amount of the fuel used during combustion.

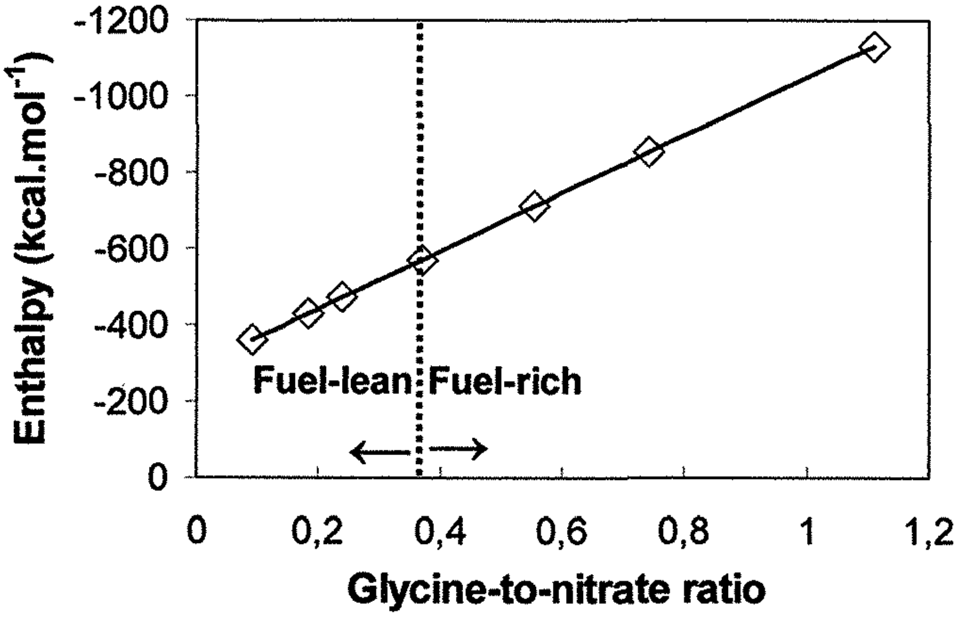


Fig. 3. Variation of enthalpy as a function of glycine-to-nitrate molar ratio.

Table 1 – Relevant thermodynamics data

Compound	ΔH_f (kcal mol^{-1})	Cp (Cal mol^{-1}K^{-1})
$Ni(NO_3)_2.6H_2O$ (c)	-113.50	-
NH_2CH_2COOH (c)	-79.71	-
NiO (c)	-58.40	11.30 + 0.00215 T
CO_2 (g)	-94.051	10.34 + 0.00274 T
N_2 (g)	0	6.50 + 0.0010 T
O_2 (g)	0	5.92 + 0.00367 T
H_2O (g)	-57.796	7.20 + 0.0036 T
NO_2 (g)	-33.2	-

[a] (c) = Crystalline, (g) = gas. [b] T = Absolute temperature. [c] Calculated from the discrete values.

Phase formation and morphology

X-Ray Diffraction (XRD) revealed the presence of well-crystallized NiO for all glycine-to-nitrate ratios as can be noticed on Fig. 4. The Ni phase was detected only for stoichiometric and fuel-rich ratios.

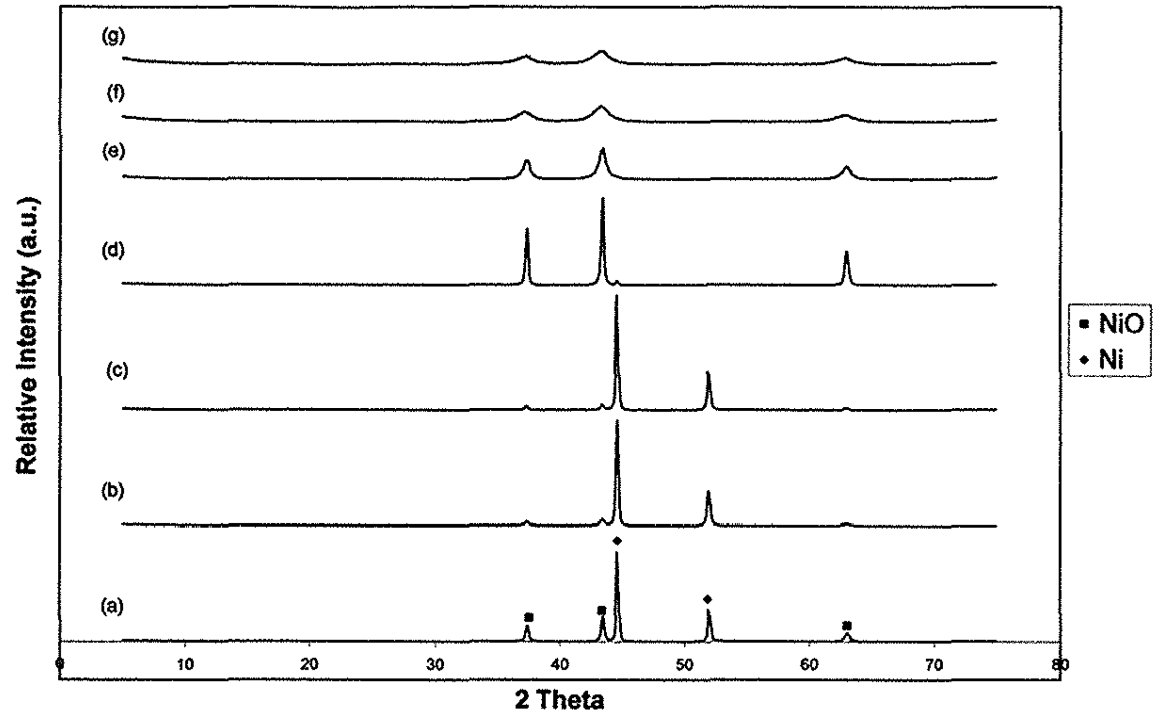


Fig. 4. X-ray diffractions of the as-synthesized powders: (a) fuel-rich (1.11), (b) fuel-rich (0.74), (c) fuel-rich (0.55) (d) stoichiometric (0.37), (e) fuel-lean (0.24) (f) fuel-lean (0.18) and (g) fuel-lean (0.09).

The NiO as single-phase was exclusively synthesized under fuel-lean ratios. It is attributed to the fact that those reactions were carried out under an oxidant condition. In the case of fuel-rich ratios, the reducing condition allowed to grow the nickel metallic phase.

The amount of fuel employed definitely plays an important, perhaps crucial role, in the determination of the properties of NiO synthesized by solution combustion synthesis.

Crystallite sizes are presented in Fig. 5. The lowest crystallite sizes were obtained under lean glycine-to-nitrate ratios. It is attributed to a decrease in flame temperature, which difficult crystal growth. In the case of stoichiometric formulation the powder synthesized was not nanometric.

There is a correlation between the increase in crystallite size as a function of fuel content in the case of glycine-nitrate combustion. Many authors have already observed this relationship[11,12].

The morphology of the agglomerates of the as-synthesized powers is shown in Fig. 6. The formulation fuel-lean (0.09) and fuel-rich (1.11) (a and c, respectively) exhibited foamy agglomerated particles with a wide distribution. Formation of these features is attributed to the evolution of a larger amount of gas during combustion. In the figure 6b (stoichiometric formulation) a dense structure can be seen probably due a local sinterization among particles caused by the high flame temperature.

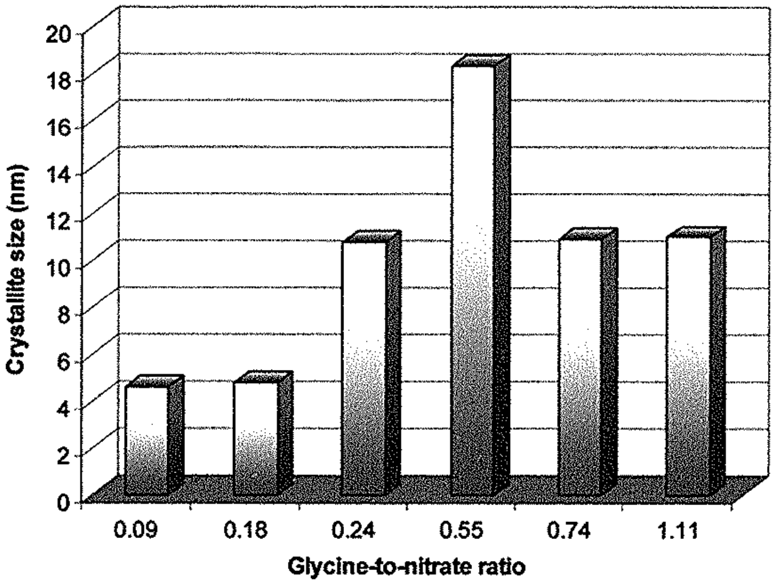
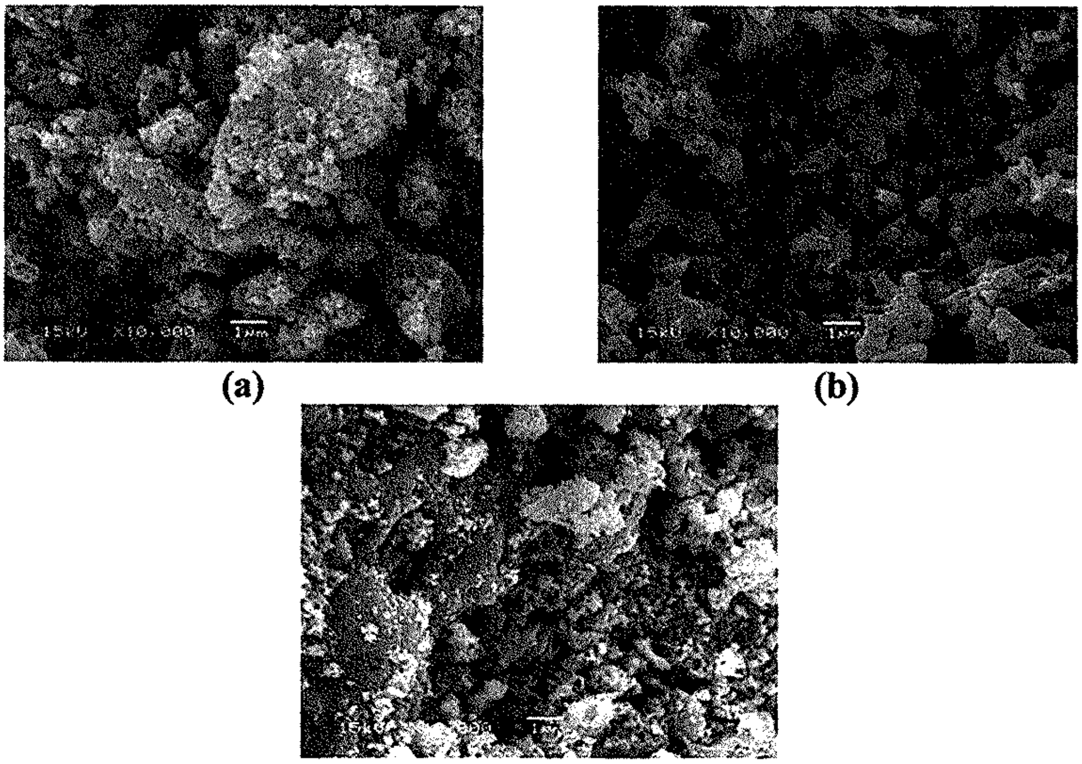


Fig. 5. Crystallite size for NiO phases under different glycine-to-nitrate ratios.



(a) (b)

(c)

Fig. 6. SEM micrographs of nickel oxide powders prepared by (a) fuel-lean (0.09), (b) stoichiometric (0.37) and (c) fuel-rich (1.11), all at 10,000X magnification.

CONCLUSION

Glycine-nitrate combustion synthesis has a potential for producing pure nanocrystalline nickel oxide powders. Optimal crystallite size could be obtained with fuel-lean molar ratio. Thermodynamic modeling of the combustion reaction shows that when glycine-to-nitrate molar ratio increases the amount of gas produced and the adiabatic flame temperature also increase.

ACKNOWLEDGEMENTS

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THE CHEMICAL ELEMENTS OF THE PERIODIC TABLE AND THE ASSOCIATED MINERALS – THE SILVER

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ABSTRACT

Silver is a natural solid with a crystalline stable structure and exhibits an abundance of 0.04 ppm (mg/kg) in the earth crust. Silver thus, like gold, is one of the chemical elements less abundant in nature. Only palladium, tellurium, platinum, ruthenium, rhodium, osmium, rhenium and iridium, present smaller geochemical distribution. However, because of its lower chemical reactivity, the metal presents a low representative in mineral constitution. This review presents a synopsis of silver minerals (129 substances) as a contribution to the scientific knowledge of these substances.

KEY WORDS: silver, mineralogy of silver; use of silver minerals.

RESUMO

A prata é um sólido natural com estrutura cristalina estável que ocorre com uma distribuição geoquímica de apenas 0,04 ppm (mg/kg) na crosta terrestre. Juntamente com o ouro é um dos elementos químicos de menor abundância na natureza. Somente o paládio, o telúrio, a platina, o rutênio, o ródio, o ósmio, o rênio e o irídio apresentam uma distribuição menor. Isto se deve à baixa reatividade química do metal, responsável pela sua pouca representatividade na constituição dos minerais. Este trabalho apresenta uma rápida sinopse dos minerais em que a prata está presente (129 substâncias), constituindo-se numa contribuição ao conhecimento científico desses compostos.

PALAVRAS-CHAVE: prata, mineralogia da prata, uso dos minerais de prata.

INTRODUCTION

Silver (derivate of the Latin *argentum*; and Greek *argyros*) is a metal known and worked by man for about 5,000 years. In the New World the first explored mines were in Zacatecas, Mexico, where the amalgamation process was developed by Bartolomé de Medina[1]. Like gold, silver is one of the chemical elements less abundant in the earth crust, with 0.04 ppm (mg/Kg). These elements are only more abundant than Pd, Pt, Te, Ru, Rh, Os, Re, and Ir. Besides its scarsity it combines with few chemical elements, because its low reactivity, thus forming a relatively small number of mineral compounds, 129 silver minerals validated until present by the IMA (International Mineralogical Association), including six new species characterized since 1999: baumstarkite, cuboargyrite, laforêtite, quadratite, sicherite, and tillmannsite)[2]. Five others species (giessenite, giraudite, incaite, tennantite, and tetrahedrite) validated before 1999[3] are not considered minerals contained silver anymore[2]. The silver is characteristically a white metal, very bulk, malleable, and ductile. Its periodical properties are: Z = 47; symbol = Ag; A = 107.87; electronic configuration: n = 5 [Kr] $4d^{10}5s^1$; Melting point = 962^{0}C; Boiling point = 1,955^{0}C; and density = 10.5. The industrial use of silver consists in jewel alloys, component for looking-glasses, batteries, chemical catalysts, photographical emulsions, films, color-glasses, and medicine. The most usual silver minerals used as industrial sources are: acanthite, silver (native silver), and pyrargyrite; others, with minor importance are: aguilarite, argyrodite, bromargyrite, chlorargyrite, crookesite, dyscrasite, empressite, eucairite, freibergite, hessite, iodargyrite, jalpaite, miargyrite, naumannite, pearceite, petzite, polybasite, proustite, stephanite, stromeyerite, and sylvanite. Other silver minerals are used like scientific matter and collections. The majority of these compounds form sulfosalts (65 species); sulfides and similar compounds (tellurides, antimonides, and selenides) make up 45 species. Only few minerals like silver, eugenite, chlorargyrite, bromargyrite, boléite, bideauxite, argentojarosite, aurorite, and wheishanite are included in other chemical classes like native elements (intermetallic alloys), halides, oxides, and others.

The main goal of the present paper is a bibliographic compilation and the scientific divulgation of the knowledge about silver mineralogy. The crystallographic constants, physical properties and geological occurrences of silver minerals can be obtained trough the Mineral Data Site and references contained in these article.

SILVER MINERALS

1.Acanthite Ag_2S – Monoclinic System – Sulfide Class – (87.06% of Ag, and 12.94% of S). Name: comes from the Greek *akanta*, due to form of its crystals; argentite was proposed by Haidinger in 1868, and comes from the Latin *argentum* which means silver[2,4,5,6,7].

2.Aguilarite Ag_4SeS – Orthorhombic System – Sulfosalt Class - (79.53% of Ag, 14.55% of Se, and 5.91% of S). Name: homage to Mr. Ponciano Aguilar (1853-1935), Former-superintendent of the San Carlos Mine, Guanajuato (Mexico)[2,8].

3.Allargentum $Ag_{1-x}Sb_x$ (x = 0.009–0.16) - Hexagonal System – Sulfide - (98.87% of Ag, and 1.13% of Sb). Name: from the Greek for *another*, and the Latin *argentum*[2,9].

4.Andorite $PbAgSb_3S_6$ – Orthorhombic System – Sulfosalt Class - (12.36% of Ag, 41.85% of Sb, 23.74% of Pb, and 22.05% of S). Name: homage to the Hungarian mineralogist Andor von Semsey (1833-1923)[2,10,11,12,13].

5.Antimonpearceite $(Ag,Cu)_{16}(Sb,As)_2S_{11}$ – Monoclinic System – Sulfosalt Class - (61.02% of Ag, 11.98% of Cu, 8.61% of Sb, 1.77% of As, and 16.63% of S). Name: derivate for its compositional relationship to pearceite[2,3,14,15].

6.Aramayoite $Ag_3Sb_2BiS_6$ – Triclinic System – Sulfosalt Class - (34.99% of Ag, 11.3% of Bi, 32.91% of Sb, and 20.8% of S). Name: homage to Mr. Felix Avelino Aramayo, Former-director of the Companhia Aramayo de Minas (Bolivia)[2,16,17].

7.Arcubisite Ag_6CuBiS_4 - (?) System – Sulfosalt Class - (6.17% of Ag, 6.01% of Cu, 15.8% of Bi and 12.12% of S, with impurities of Fe 0.53%, Te 2.41%, and Pb 1.96%). Name: derivate of the Latin/German compositions: *argentum* (silver) + *cuprum* (copper) + *wismut* (bismuth) + *sulfur* (sulfur)[2,18].

8.Argentojarosite $AgFe_3(SO_4)_2(OH)_6$ – Trigonal System – Sulfate Class - (18.94% of Ag, 29.41% of Fe, 11.26% of S, and 39.33% of O). Name: derivate for its compositional relationship to jarosite[2,3,19].

9.Argentopentlandite $Ag(Fe,Ni)_8S_8$ – Cubic System – Sulfide Class – (13.21% of Ag, 11.02% of Fe, 14.37% of Ni, and 31.40% of S). Name: derivate for its compositional relationship to pentlandite[2,3,20].

10.Argentopyrite $AgFe_2S_3$ – Orthorhombic System – Sulfide Class - (34.16% of Ag, 35.37% of Fe, and 30.47% of S). Name: derivate for its compositional relationship to pyrite[2,21,22].

11.Argentotennantite $Ag_6Cu_4(Zn,Fe)_2(As,Sb)_4S_{13}$ – Cubic System – Sulfosalt Class - (43.56% of Ag, 8.55% of Cu, 5.28% of Zn, 1.5% of Fe, 12.1% of As, 6.56% of Sb, and 22.44% of S). Name: derivate for its compositional relationship to tennantite[2,3,23].

12.Argyrodite Ag_8GeS_6 – Orthorhombic System – Sulfide Class - (76.5% of Ag, 6.44% of Ge, and 17.06% of S, with impurities of Ga). Name: comes from the Greek *argyros* which means rich in silver[2].

13.Arsenpolybasite $(Ag,Cu)_{16}(As,Sb)_2S_{11}$ – Monoclinic System – Sulfosalt Class - (62.39% of Ag, 12.25% of Cu, 2.93% of Sb, 5.42% of As, and 17% of S). Name: derivate for its compositional relationship to polybasite[2,14,24].

14.Aurorite $(Mn^{2+},Ag,Ca)Mn^{4+}{}_3O_7.3H_2O$ – Trigonal System – Oxide Class - (8.12% of Ag, 48.23% of Mn, 2.01% of Ca, 1.52% of H, and 40.13% of O). Name: reference to the Aurora mine (USA)[2,25].

15.Balkanite $Cu_9Ag_5HgS_8$ – Orthorhombic System – Sulfide Class - (34.39% of Ag, 36.47% of Cu, 12.79% of Hg, and 16.36% of S). Name: reference to the Balkan Peninsula (Bulgaria)[2,26].

16.Baumhauerite-2a $Pb_{11}Ag(As,Sb)_{18}S_{36}$ – Monoclinic System – Sulfosalt Class - (51.38% of Pb, 24.77% (?) of Ag, As, Sb, and 23.85% of S). Name: homage to the German mineralogist Adolph Baumhauer (1848-1926)[2,27].

17.Baumstarkite $AgSbS_2$ – Triclinic System – Sulfosalt Class; (37.22% of Ag, 38.5% of Sb, 2.15% of As, and 22.13% of S). Name: homage to the German mineralogist Manfred Baumstark[2,16].

18.Benjaminite $Ag_3Bi_7S_{12}$ – Monoclinic System – Sulfosalt Class - (2.23% of Ag, 11.37% of Ag, 48.95% of Bi, 19.41% of Pb, and 18.03% of S). Name: homage to the American mineralogist Marcus Benjamin (1857-1932)[2,28].

19.Benleonardite $Ag_8(Sb,As)Te_2S_3$ – Tetragonal System – Sulfosalt Class - (65.74% of Ag, 4.64% of Sb, 19.44% of Te, 2.85% of As, and 7.33% of S). Name: homage to the American geologist Benjamin F. Leonard[2,23,29].

20.Berryite $Pb_3Bi_7(Ag,Cu)_5S_{16}$ – Monoclinic System – Sulfosalt Class - (8.91% of Ag, 5.25% of Cu, 48.34% of Bi, 20.54% of Pb, and 16.95% of S). Name: homage to the Canadian mineralogist Leonard Gascoigne Berry (1914-1982)[2,30].

21.Bideauxita $Pb_2AgCl_3(F,OH)$ – Cubic System – Halide Class - (16.21% of Ag, 0.08% of H, 62.26% of Pb, 15.96% of Cl, 1.2% of O, and 4.28% of F). Name: homage to the American mineralogist Richard August Bideaux (1935-2004)[2,31].

22.Billingsleyite $Ag_7(As,Sb)S_6$ – Orthorhombic System – Sulfosalt Class - (73.85% of Ag, 7.33% of As, and 18.82% of S). Name: homage to the American mineralogist Paul Billingsley (1867-1962)[2,32].

23.Bohdanowiczite $AgBiSe_2$ – Hexagonal System – Sulfosalt Class - (22.72% of Ag, 44.02% of Bi, and 33.26% of Se). Name: homage to the Polish geologist Karol Bohdanowicz (1864-1947)[2,33].

24.Boléite $KPb_{26}Ag_9Cu_{24}Cl_{62}(OH)_{48}$ – Cubic System – Halide Class - (8.88% of Ag, 0,36% of K, 13.94% of Cu, 0.44 of H%, 49.26% of Pb, 7.02% of O, and 20.1% of Cl). Name: homage to the locality of Boleo mine (Mexico)[2,33,34].

25.Borodaevite $Ag_5(Fe,Pb)Bi_7(Sb,Bi)_2S_{17}$ – Monoclinic System – Sulfosalt Class - (19.71% of Ag, 51.54% of Bi, 10.01% of Sb, and 18.75% of S). Name: homage to the Russian mineralogist Yuri Borodaev[2].

26.Bromargyrite AgBr – Cubic System – Halide Class - (57.45% of Ag, and 42.55% of Br). Name after its chemical composition[2,4].

27.Cameronite $AgCu_7Te_{10}$ – Tetragonal System – Sulfide Class - (5.9% of Ag, 24.32% of Cu, and 69.78% of Te). Name: homage to the American economic geologist Eugene Cameron[2,35].

28.Canfieldite Ag_8SnS_6 – Orthorhombic System – Sulfide Class - (73.5% of Ag, 10.11% of Sn, and 16.39% of S). Name: homage to the American mining engineer Frederick Canfield (1849-1926)[2].

29.Capgarronite HgS.Ag(Cl,Br,I) – Orthorhombic System – Sulfide/Halide Classes. (?%). Name: reference to the Cap Garrone mine (France)[2,36].

30.Cervelleite Ag_4TeS – Cubic System – Sulfosalt Class – (72.99% of Ag, 21.59% of Te, and 5.42% of S). Name: homage to the French mineralogist Bernard Cerveille[2,37].

31.Chlorargyrite AgCl – Cubic System – Halide Class - (75.26% of Ag, and 24.74% of Cl). Name: after its chemical composition (Greek *chloros* = *pale green*; Latin *argentums;* Greek, *argyros*)[2,4,38].

32.Chrisstanleyite $Ag_2Pd_3Se_4$ – Monoclinic System – Sulfide Class - (25.36% of Ag, 37.52% of Pd, and 37.12% of Se). Name: homage to the British mineralogist Chriss Stanley[2,39,40].

33.Criddleite $TlAg_2Au_3Sb_{10}S_{10}$ – Monoclinic System – Sulfosalt Class - (8.46% of Ag, 8.02% of Tl, 47.76% of Sb, 23.18% of Au, and 12.58% of S). Name: homage to the English mineralogist Alan Criddle (1944-2002)[2,41].

34.Crookesite $Cu_7(Tl,Ag)Se_4$ – Tetragonal System - Sulfide Class - (2.87% of Ag, 16.29% of Tl, 47.28% of Cu, and 33.57% of Se). Name: homage to the English chemist Sir William Crookes (1832-1919)[2,23].

35.Cuboargyrite $AgSbS_2$ – Cubic System - Sulfosalt Class - (41.22% of Ag, 46.53% of Sb, and 5% of S). Name: alludes to the polymorphic relationship with miargyrite[2,42].

36.Cupropavonite $AgPbCu_2Bi_5S_{10}$ – Monoclinic System – Sulfosalt Class - (5.97% of Ag, 7.03% of Cu, 57.8% of Bi, 11.46% of Pb, and 17.74% of S). Name after its similarity with pavonite[2,43].

37.Danielsite $(Cu,Ag)_{14}HgS_8$ – Orthorhombic System – Sulfide Class - (28.31% of Ag, 41.7% of Cu, 13.16% of Hg, and 16.83% of S). Name: homage to the American mineral collector John L. Daniels[2,44].

38.Dervillite Ag_2AsS_2 – Monoclinic System – Sulfosalt Class – (60.81% of Ag, 21.12% of As, and 18.08% of S). Name: homage to the French mineralogist Prof. Dr. Henri Derville[2].

39.Diaphorite $Pb_2Ag_3Sb_3S_8$ – Monoclinic System – Sulfosalt Class - (23.8% of Ag, 26.86% of Sb, 30.48% of Pb, and 18.87% of S). Name: derivate from the Greek diaphora = *difference*[2,6,45].

40.Dyscrasite Ag_3Sb – Orthorhombic System – Sulfide Class - (72.66% of Ag, and 27.34% of Sb). Name: comes from the Greek meaning "bad alloy"[2,45,46].

41.Empressite AgTe – Orthorhombic System – Sulfide Class - (45.81% of Ag, and 54.19% of Te). Name: derivate from the Empress Josephine Mine (USA)[2,47,48,49,50].

42.Eskimoite $Ag_7Pb_{10}Bi_{15}S_{36}$ – Monoclinic System – Sulfosalt Class - (61% of Ag, 44.05% of Bi, 29.12% of Pb, and 16.22% of S). Name: homage to the Eskimos, the natives of the Greenland[2,13,51].

43.Eucairite CuAgSe – Orthorhombic System – Sulfide Class - (43.08% of Ag, 25.38% of Cu, and 31.54% of Se). Name: comes from the Greek for "opportunity", because it was discovered shortly after discovered of the Se[2].

44.Eugenite $Ag_{11}Hg_2$ – Cubic System – Native Elements - (70.76% of Ag, and 29.24% of Hg). Name: homage to the Austrian mineralogist Eugen Friedrich Stumptl[2,52].

45.Fettelite $Ag_{24}HgAs_5S_{20}$ – Trigonal System – Sulfosalt Class - (68.03% of Ag, 5.27% of Hg, 9.84% of As, and 16.85% of S). Name: homage to the German M. Fettel, a mineral collector[2].

46.Fischesserite Ag_3AuSe_2 – Cubic System - Sulfide Class - (47.69% of Ag, 29.03% of Au, and 23.28% of Se). Name: homage to the French mineralogist Raymond Fischesser[2,53].

47.Fizélyite $Pb_{14}Ag_5Sb_{21}S_{48}$ – Monoclinic System – Sulfosalt Class - (7.16% of Ag, 33.93 of Sb, 38.49% of Pb and 20.42% of S). Name: homage to the Hungarian mineralogist Sandor Fyzély[2,13].

48.Freibergite $Ag_6Cu_4(Fe,Zn)_2Sb_4S_{13}$ – Cubic System – Sulfosalt Class - (3.47% of Fe, 3.88% of Zn, 11.86% of Cu, 40.25% of Ag, 18.93% of Sb, and 21.6% of S). Name: reference from Freiberg, the site where the mineral was firstly found[2,3,4,45].

49.Freieslebenite $PbAgSbS_3$ – Monoclinic System – Sulfosalt Class - (38.87% of Pb, 20.24% of Ag, 22.84% of Sb, and 18.05% of S); compare with laffittite and marrite. Name: homage to the German mineralogist Johann Karl Freiesleben (1774-1846), mining commissioner of Saxony[2,54].

50.Furutobeite $(Cu,Ag)_6PbS_4$ – Monoclinic System – Sulfide Class - (?%). Name: reference to Furutobe Mine (Japan)[2,55].

51.Geffroyite $(Cu,Fe,Ag)_9(Se,S)_8$ – Cubic System – Sulfide Class - (3.74% of Fe, 12.78% of Cu, 43.4% of Ag, 35.3% of Se, and 4.78% of S). Name: homage to the French metallurgist Jacques Geffroy[2,3,56].

52.Gustavite $PbAgBi_3S_6$ - Monoclinic System – Sulfosalt Class - (9.51% of Ag, 55.27% of Bi, 18.27% of Pb, and 16.96% of S). Name: homage to the Danish chemist engineer Gustav Hageman (1842-1916)[2,57].

53.Hatchite $(Pb,Tl)_2AgAs_2S_5$ – Triclinic System – Sulfosalt Class - (12.30% of Tl, 12.98% of Ag, 18.03% of As, 37.40% of Pb, and 19,29% of S). Name: homage to the British geologist and mining engineer Frederick H. Hatch (1864-1932)[2,58].

54.Henryite $Cu_4Ag_3Te_4$ – Cubic System – Sulfide Class - (23.36% of Cu, 29.74% of Ag, and 46.90% of Te). Name: homage to the English mineralogist Dr. Normann F. M. Henry (1864-1932)[2,59].

55.Hessite Ag_2Te – Monoclinic System – Sulfide Class - (45.81% of Ag, and 54.19% of Te). Name: homage to the Swiss chemist G. H. Hesse (1802-1850)[2,60].

56.Heyrovskýite $(Pb,Ag)_5Bi_3S_8$ – Orthorhombic System – Sulfosalt Class - (2.84% of Ag, 27.48% of Bi, 54.50% of Pb and 18.50% of S). Name: homage to the Czech chemist J. Heyrovsky (1890-1967)[2,61].

57.Hocartite Ag_2FeSnS_4 – Tetragonal System – Sulfide Class - (41.60% of Ag, 10.77% of Fe, 22.89% of Sn, and 24.73% of S). Name: homage to the French mineralogist Raymind Hocart[2,3,62].

58.Iltisite $HgSAg(Cl,Br)$ – Hexagonal System – Sulfide Class - (51.82% of Hg, 8.28% of S, 27.87% of Ag, 6.87% of Cl, and 5.16% of Br). Name: homage to the French mineral collector Antoine Iltis[2,63,64].

59.Imiterite Ag_2HgS_2 – Monoclinic System – Sulfide Class - (44.90% of Ag, 41.75% of Hg, and 13.35% of S). Name: reference from Imiter Mine (Morocco)[2].

60.Iodargyrite AgI – Hexagonal System – Iodide Class (45.95% of Ag, and 54.05% of I). Name: derivate of chemical composition: iodine + Greek (*argyros*) = silver[2,3,4,65,66,67].

61.Jalpaite Ag_3CuS_2 – Tetragonal System – Sulfide Class - (14.08% of Cu; 71.71% of Ag, and 14.21% of S). Name: reference to Jalpa Mine, Zacatecas (Mexico)[2,68].

62.Krennerite $(Au,Ag)Te_2$ – Orthorhombic System – Sulfide Class (56.44% of Te, 43.46% of Au, and traces of Ag). Name: homage to the Hungarian mineralogist Joseph A. Krenner (1839-1920)[2,4,60,69].

63.Kutínaite $Cu_{14}Ag_6As_7$ – Cubic System – Sulfide Class (43.85% of Cu, 31.02% of Ag, and 25.13% of As). Name: homage to the Czech mineralogist Jan Kutina[2,70,71].

64.Laffittite $AgHgAsS_3$ – Monoclinic System – Sulfosalt Class – (22.49% of Ag, 41.83% of Hg, 15.62% of S, and 20.06% of S). Name: homage to the French mineralogist Pierre Laffitti, Director of National School of Mines, Paris[2,72,73,74].

65.Laforêtite $AgInS_2$ – Tetragonal System – Sulfide Class – (40.03% of In, 37.61% of Ag, and 22.36% of S). Name: homage to the French metallographer Claude Laforêt[2,75,76].

66.Larosite $(Cu,Ag)_{21}(Pb,Bi)_2S_{13}$ – Orthorhombic System – Sulfosalt Class (53.51% of Cu, 9.56% of Ag, 9.26% of Bi, 9.18% of Pb, and 18.48% of S). Name: homage to the Canadian mineralogist Fred La Rose[2,77].

67.Lenaite $AgFeS_2$ – Tetragonal System – Sulfide Class; (24.51% of Fe, 47.34% of Ag, and 28.15% of S). Name: reference to Lena River (Russia)[2].

68.Lengenbachite $Pb_6(Ag,Cu)_2As_4S_{13}$ – Triclinic System – Sulfosalt Class – compare with cylindrite; (2.38% of Cu, 6.05% of Ag, 14.00% of As, 58.09% of Pb, and 19.48% of S). Name: reference from Lengenbach Quarry (Switzerland)[2,78].

69.Luanheite Ag_3Hg – Hexagonal System – Native Elements Class – (61.73% of Ag, and 38.27% of Hg). Name: reference to Luanhe River (People's Republic of China)[2,79].

70.Makovickyite $Ag_{1.5}Bi_{5.5}S_9$ – Monoclinic System – Sulfosalt Class – (10.11% of Ag, 71.85% of Bi, and 18.04% of S. Name: homage to the Danish mineralogist Prof. Dr. Emil Makovicky of University of Copenhagen[2].

71.Marrite $PbAgAsS_3$ – Monoclinic System – Sulfosalt Class – (22.19% of Ag, 15.41% of As, 42.62% of Pb, and 19.79% of S). Name: homage to the British geologist John Edward Marr (1857-1933)[2].

72.Matildite $AgBiS_2$ – Trigonal System – Sulfosalt Class – (28.31% of Ag, 54.85% of Bi, and 16.83% of S). Name: reference to the Matilda Mine (Peru)[2,16].

73.Mckinstryite $(Ag,Cu)_2S$ – Orthorhombic System – Sulfide Class – (23.94% of Cu, 60.96% of Ag, and 15.10% of S). Name: homage to the American economic geologist Hug Mckinstry (1896-1961)[2,80].

74.Miargyrite $AgSbS_2$ – Monoclinic System – Sulfosalt Class – (36.72% of Ag, 41.45% of Sb, and 21.83% of S). Name: comes from the Greek *meion* (minor) + *argyros* (silver) which means minor quatity of silver what the proustite, and pyrargyrite[2,16,17,44,81,82,83].

75.Miersite $(Ag,Cu)I$ – Cubic System – Iodide Class – (7.10% of Cu, 36.17% of Ag, and 56.73% of I). Name: homage to the British mineralogist Henry Alexander Miers (1848-1942) of the Oxford University[2,67,84].

76.Moschellandsbergite Ag_2Hg_3 – Cubic System – Native Elements – (26.39% of Ag, and 73.61% of Hg). Name: reference from Moschellandsberg (Germany)[2,84].

77.Mummeite $Ag_2CuPbBi_6S_{13}$ – Monoclinic System - Sulfosalt Class – (2.81% of Cu, 14.29% of Ag, 55.36% of Bi, 9.15% of Pb, and 18.4% of S). Name: homage to the Australian mineralogist William G. Mumme[2].

78.Muthmannite $(Ag,Au)Te$ – Monoclinic System (?) – Sulfide Class - (19.18% of Ag, 46.51% of Te, and 34.31% of Au); Name: homage to the German crystallographer and chemist Friedrich W. Muthmann (1861-1913)[2,4].

79.Naumannite Ag_2Se – Orthorhombic System – Sulfide Class – (73.21% of Ag, and 26.79% of Se); Name: homage to the German crystallographer and mineralogist Carl Friedrich Naumann (1797-1873)[2,85].

80.Neyite $Pb_7(Cu,Ag)_2Bi_6S_{17}$ – Monoclinic System – Sulfosalt Class – (2.88% of Cu, 1.63% of Ag, 41.04% of Bi, 37.88% of Pb, and 16.57% of S). Name: homage to the Canadian geologist Charles Stewart Ney (1918-1975)[2,86].

81.Novákite $(Cu,Ag)_{21}As_{10}$ – Monoclinic System – Sulfide Class - (55.58% of Cu, 9.93% of Ag, and 34.49% of As); Name: homage to the Czech mineralogist Jiri Novák (1902-1971)[2,87].

82.Ourayite $Ag_3Pb_4Bi_5S_{13}$ (?) – Orthorhombic System – Sulfosalt Class – (12.96% of Ag, 41.16% of Bi, 29.86% of Pb, and 16.02% of S); Name: reference to Ouray Mine (USA)[2,88,89,90].

83.Owyheeite $Ag_3Pb_{10}Sb_{11}S_{28}$ – Orthorhombic System – Sulfosalt Class – (6.24% of Ag, 12.09% of Bi, 21.14% of Sb, 41.97% of Pb, and 18.56% of S). Name: after its locality of Owyheei (USA)[2,91].

84.Paděraite $AgPb_2Cu_6Bi_{11}S_{22}$ – Monoclinic System – Sulfosalt Class – (9.76% of Cu, 2.76% of Ag, 58.53% of Pb, and 18.05% of S); Name: homage to the Czech mineralogist K. Padera[2].

85.Paraschachnerite $Ag_{1.2}Hg_{0.8}$ – Orthorhombic System – Native Elements Class - (44.65% of Ag, and 55.35% of Hg); Name: for its relationship to schachnerite[2,92].

86.Pavonite $AgBi_3S_5$ – Monoclinic System – Sulfosalt Class – (1.80% of Cu, 9.16% of Ag, 53.27% of Bi, 17.60% of Pb, and 18.16% of S). Name: homage to the Canadian mineralogist Martin Alfred Peacock (1898-1950)[2,93].

87.Pearceite $(Ag,Cu)_{16}As_2S_{11}$ - Monoclinic System – Sulfosalt Class – (77.45% of Ag, 6.72% of As, and 15.83% of S). Name: homage to the American chemist and metallurgist Richard Pearce (1837-1927)[2,14,24].

88.Penzhinite $(Ag,Cu)_4Au(S,Se)_4$ – Hexagonal System – Sulfide Class – (8.37% of Cu, 42.62% of Ag, 25.94% of Au, 10.40% of Se, and 12.67% of S); Name: reference to Penzhina River (Russia)[2,94].

89.Perroudite $Hg_5Ag_4S_5(Cl,I,Br)_4$ – Orthorhombic System – Halide Class – (22.78% of Ag, 52.94% of Hg, 6.77% of S, 10.72% of I, 3.80% of Br, and 2.99% of Cl); Name: homage to Pierre Perroud, Professor at Voltaire College, Geneva, Switzerland[2,95,96,97].

90.Petrovskaite $AuAg(S,Se)$ – Monoclinic System – Sulfide Class (31.80% of Ag, 58.06% of Au, 1.16% of Se, and 8.98% of S); Name: homage to the Russian mineralogist Nina Petrovskaya[2,7,98].

91.Petzite Ag_3AuTe_2 – Cubic System – Sulfide Class – (41.71% of Ag, 32.90% of Te, and 25.39% of Au); compare with fischesserite. Name: homage to the chemist W. Petz, discoverer of the mineral[2,4,60,99].

92.Pirquitasite Ag_2ZnSnS_4 – Tetragonal System – Sulfide Class – (12.38% of Zn, 40.85% of Ag, 22.48% of Sn, and 24.29% of S); forms a series with hocartite. Name: reference to the Pirquitas Mine (Argentina)[2,3,100].

93.Polybasite $(Ag,Cu)_{16}Sb_2S_{11}$ – Monoclinic System – Sulfosalt Class – (11.85% of Cu, 60.35% of Ag, 11.35% of Sb, and 16.45% of S); forms a series with pearceite; compare with antimonpearceite. Name: comes from the Greek *polys* (very) + *basis* (basis)[2,14,24].

94.Proustite Ag_3AsS_3 – Trigonal System – Sulfosalt Class – (65.41% of Ag, 15.14% of As, and 18.44% of S); forms a solid-solution with pyrargyrite; dimorphism with xanthoconite. Name: homage to the French chemist J. L. Proust (1755-1826)[2,4,6,101].

95.Pyrargyrite Ag_3SbS_3 – Trigonal System – Sulfosalt Class – (59.75% of Ag, 22.48% of Sb, and 17.76% of S); dimorphism with pyrostilpnite; forms a solid-solution with proustite. Name: pyrargyrite comes from the Greek *pyr* (fire) + *argyros* (silver)[2,4,6,45,101].

96.Pyrostilpnite Ag_3SbS_3 – Monoclinic System – Sulfosalt Class – (59.75% of Ag, 22.48% of Sb, and 17.76% of S); dimorphism with pyrargyrite. Name: comes from the Greek *pyr* (fire) + *stilpnos* (brilliant)[2,6,102].

97.Quadradite $Ag(Cd,Pb)(As,Sb)S_3$ – Tetragonal System – Sulfosalt Class – (21.91% of Cd, 26.29% of Ag, 18.26% of As, 10.10% of Pb, and 23.44% of S). Name: derived from the conspicuous quadratic shape of the mineral[2,103].

98.Ramdorhite $Ag_3Pb_6Sb_{11}S_{24}$ – Monoclinic System – Sulfosalt Class – (8.80% of Ag, 36.44% of Sb, 33.82% of Pb, and 20.94% of S); compare with andorite. Name: homage to the German mineralogist Paul Ramdohr[2,12,13].

99.Rayite$(Ag,Tl)_2Pb_8Sb_8S_{21}$ – Monoclinic System – Sulfosalt Class – (2.86% of Tl, 4.53% of Ag, 27.29% of Sb, 46.44% of Pb, and 18.87% of S); compare with semseyite. Name: homage to the Indian mineralogist Santosh K. Ray[2,104].

100.Roshchinite $Ag_{19}Pb_{10}Sb_{51}S_{96}$ - Orthorhombic System – Sulfosalt Class – (0.99% of Cu, 15.90% of Ag, 43.46% of Sb, 2.91% of As, 12.86% of Pb, and 23.89% of S). Name: homage to the Russian geologist Yuri Roschin (1934-1979)[2].

101.Samsonite $Ag_4MnSb_2S_6$ – Monoclinic System – Sulfosalt Class – (5.96% of Mn, 46.78% of Ag, 26.40% of Sb, and 20.86% of S). Name: reference from Samson Mine(USA)[2,105].

102.Schachnerite $Ag_{1.1}Hg_{0.9}$ – Hexagonal System – Native Elements Class – (39.66% of Ag, and 60.34% of Hg). Name: homage to the German mineralogist Doris Schachner (1904-1989)[2,106].

103.Schirmerite $Ag_3Pb_3Bi_9S_{18}$ to $Ag_3Pb_6Bi_7S_{18}$ – Orthorhombic System – Sulfosalt Class – (10.84% of Ag, 49.00% of Bi, 20.82% of Pb, and 19.33% of S); Name: homage to Former-superintendent J. H. L. Schirmer of the U. S. Mint, Denver, Colorado (USA)[2,82,89,90,107,108].

104.Selenostephanite $Ag_5Sb(Se,S)$ – Orthorhombic System – Selenide Class – (57.99% of Ag, 13.09% of Sb, 25.47%). Name: reference to the compositional similiraty to stephanite[2].

105.Sicherite $TlAg_2(As,Sb)_3S_6$ – Orthorhombic System – Sulfosalt Class – (23.27% of Tl, 24.56% of Ag, 11.09% of Sb, 19.19% of As, and 21.90% of S). Name: homage to the Swiss syndicalist Valentin Sicher[2,109].

106.Silver (Native silver) Ag – Cubic and Hexagonal Systems – Native Elements – forms a series with gold, the -3C, -2H and -4H polytypes are knowns[2,4,6,110,111].

107.Smithite $AgAsS_2$ – Monoclinic System – Sulfosalt Class – (43.69% of Ag, 30.34% of As, and 25.97% of S). Name: homage to the British crystallographer Herbert Smith (1872-1953)[2].

108.Sopcheite $Ag_4Pd_3Te_4$ – Orthorhombic System – Sulfide Class – (34.21% of Ag, 40.47% of Te, and 25.32% of Pd); Name: reference from Sopcha Massif(Russia)[2,112].

109.Stephanite Ag_5SbS_4 – Orthorhombic System – Sulfosalt Class – (68.33% of Ag, 15.42% of Sb, and 16.25% of S). Name: homage to the Austrian Archduke Victor Stephan (1817-1867) Former Mining Director[2,6,113].

110.Sternbergite $AgFe_2S_3$ – Orthorhombic System – Sulfide Class – (35.37% of Fe, 34.16% of Ag, and 30.47% of S). Name: homage to the Czech mineralogist Caspar Maria Sternberg[2,22,114,115].

111.Sterryite $Ag_2Pb_{10}(Sb,As)_{12}S_{29}$ – Orthorhombic System – Sulfosalt Class – (4.75% of Ag, 24.15% of Sb, 4.,95% of As, 45.66% of Pb, and 20.49% of S). Name: homage to the Canadian mineralogist T. Sterry Hunt (1826-1892)[2,116].

112.Stetefeldtite $Ag_2Sb_2O_5(OH)_2$ - Cubic System – Oxide Class – (37.73% of Ag, 42.59% of Sb, 0.09% of H, and 19.59% of O). Name: homage to the German-American mining engineer Carls Stetefeldt (1838-1896)[2].

113.Stromeyerite AgCuS – Orthorhombic System – Sulfide Class - (31.23% of Cu, 53.01% of Ag, and 15.76% of S); Name: homage to the German mineralogist and chemist Friedrich Stromeyer[2].

114.Stützite $Ag_{5-x}Te_3$ – Hexagonal System – Sulfide Class - (56.98% of Ag, and 43.02% of Te). Name: homage to the Austrian mineralogist Andreas Stutz (1747-1806)[2,47,48,49].

115.Sylvanite $AuAgTe_4$ – Monoclinic System – Sulfide Class – (6.27% of Ag, 59.36% of Te, and 34.36% of Au). Name: comes from the Latim *silvanium* which means tellurium and Transylvania (Romania)[2,4,60].

116.Telargpalite $(Pd,Ag)_3Te$ (?) – Cubic System – Sulfide Class – (4.82% of Ag, 28.54% of Te, and 66.64% of Pd). Name: for the composition (Te, Ag and Pd)[2,117].

117.Tillmannsite $(Ag_3Hg)(V,As)O_4$ – Tetragonal System – Oxide Class – (0.17% of V, 1.60% of Ag, 97.77% of Hg, 0.13% of As, and 0.33% of O). Name: homage to the Austrian mineralogist Ekkhart Tillsmanns[2,118].

118.Toyohaite $Ag_2FeSn_3S_8$ – Tetragonal System – Sulfide Class – (6.32% of Fe, 24.40% of Ag, 40.28% of Sn, and 29.01% of S). Name: reference from Toyo Mine (Japan)[2].

119.Treasurite $Ag_7Pb_6Bi_{15}S_{32}$ – Monoclinic System - Sulfosalt Class – (12.26% of Ag, 50.90% of Bi, 20.18% of Pb, and 16.66% of S). Name: reference from Treasure Mine (USA)[2,107,108].

120.Trechmannite $AgAsS_2$ – Trigonal System – Sulfosalt Class – (43.69% of Ag, 30.34% of As, and 25.97% of S). Name: homage to the English mineralogist Charles Trechmenn (1851-1917)[2].

121.Tsnigriite $Ag_9SbTe_3(S,Se)_3$ – Monoclinic System – Sulfosalt Class – (60.87% of Ag, 7.63% of Sb, 24.00% of Te, 2.48% of Se, and 5.03% of S). Name: from the initials of the Russian denomination for the Central Scientific-Research Institute of Geological Prospecting in Moscow[2].

122.Uchucchacuaite $AgPb_3MnSb_5S_{12}$ – Orthorhombic System – Sulfosalt Class – (3.09% of Mn, 6.07% of Ag, 34.24% of Sb, 34.96% of Pb, and 21.64% of S). Name: reference from Uchuc-Chacuaia Region (Peru)[2,12,119].

123.Uytenbogaardtite Ag_3AuS_2 – Tetragonal System – Sulfide Class – (55.35% of Ag, 33.69% of Au and, 10.97% of S). Name: homage to the Dutch mineralogist Willem Uytenbogaardt (1818-?)[2,4,6].

124.Vikingite $Ag_5Pb_8Bi_{13}S_{30}$ – Monoclinic System – Sulfosalt Class – (9.18% of Ag, 46.24% of Bi, 28.21% of Pb, and 16.37% of S). Name: reference to the Vikings[2,108,109].

125.Volynskite $AgBiTe_2$ – Hexagonal System – Sulfosalt Class – (2.86% of Ag, 35.53% of Bi, and 44.61% of Te). Name: homage to the Polish economic geologist mineralogist I. S. Volynskii (1900-1947)[2].

126.Wallisite $PbTl(Cu,Ag)As_2S_5$ – Triclinic System – Sulfosalt Class – (25.66% of Tl, 5.98% of Cu, 3.39% of Ag, 18.82% of As, 26.02% of Pb and 20.13% of S). Name: was proposed in reference to Wallis (Switzerland)[2,120].

127.Weishanite$(Au,Ag)_{1.2}Hg_{0.8}$ – Hexagonal System – Native Elements Class – (8.74%

of Ag, 43.36% of Hg, and 47.90% of Au). Name: reference from Weihan Province (People's Republic of China)[2].

128.Xanthoconite Ag_3AsS_3 – Monoclinic System – Sulfosalt Class – (65.41% of Ag, 15.14% of As, and 19.44% of S). Name: comes from the Greek *xanthos* which means yellow, and *khroa,* which means color[2].

129.Zoubekite $AgPb_4Sb_4S_{10}$ – Orthorhombic System – Sulfosalt Class (6.18% of Ag, 27.92% of Sb, 47.51% of Pb, and 18.38% of S). Name: homage to the Czech geologist Vladimir Zoubek[2].

CONCLUSIONS

The relatively small number of silver minerals (129 species described and validated by IMA – International Mineralogical Association) is related to the low chemical reactivity of the chemical element. Only the pyrargyrite, the silver (native silver), the tetrahedrite, the tennantite and the acanthite are industrial sources of the metal, that also can be obtained as a subproduct of the copper, lead and zinc sulfides.

The majority of silver minerals are Sulfosalts and sulfides, originated by hydrothermal process in ore veins.

The main silver producers on a global scale are: Mexico and Canada; but the countries with major bulk reserves are: Canada, Mexico, USA, Australia, and Peru[121]. Brazil does not present important argentiferous deposits, a few silver deposits occurring in restricted regions of the Minas Gerais, São Paulo, Paraná, Bahia, and Goiás states. Silver, as subproduct can be obtained from lead, zinc and copper mines in São Paulo, Paraná, Santa Catarina, Bahia, and Rio Grande do Sul (Santa Maria mine, Minas do Camaquã, Caçapava do Sul) states.

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ELIMINATION AND CONTROL OF AQUATIC PESTS IN THE ENVIRONMENT

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ABSTRACT

The present paper is a brief review of possible methods that can be used to control or eliminate aquatic pests from the environment, with particular emphasis on the golden mussel, ***Limnoperna fortunei (Dunker 1856)****. This bivalve mollusk, native of Southeast Ásia, has infested most of the rivers in Northern Argentina, Uruguay, Paraguay and Southern Brazil and is causing serious environmental difficulties and biofouling. In addition, it causes serious problems to water treatment stations and hydroeletric power plants.*

RESUMO

O presente trabalho representa uma breve análise dos métodos que podem ser usados para combater ou eliminar várias pestes aquáticas com ênfase sobre o mexilhão dourado, ***Limnoperna fortunei (Dunker 1856).*** *Este molusco bivalve, originário do Sudeste da Ásia, invadiu grande parte dos rios do norte da Argentina, Uruguai, Paraguai e sul do Brasil e está degradando o meio ambiente na região. Além disso, está causando sérios problemas no abastecimento de água e geração de energia hidroelétrica.*

KEYWORDS: Aquatic Pests, Golden Mussel, Biofouling, Hydroeletric Power Plants, Water Treatment

The present paper is a brief review of the possible methods and technologies that could be used to control or eliminate aquatic pests from the environment , with emphasis on bivalve mollusks and in particular the golden mussel, *Limnoperna fortunei* (Dunker 1856).

Major preoccupation with marine pests and negative impacts caused by exotic aquatic species began soon after World War II , although control of undesirable organisms in the environment was known since ancient times.[1-24]

Navigation and particularly the use of ballast water seem to be the main causes of infestation of ports, marinas, gulfs, estuaries and rivers throughout the world.

The methods and management technologies usually applied to control the pest species are: a) Physical-Mechanical (physical removal, destruction, fire, etc) b) Chemical (organic and inorganic pesticides or biocides) and c) Biological (habitat, predators, pathogens, parasites and genetic manipulation).[1-4]

The more common aquatic species involved include toxic phytoplankton, macroalgae, ctenophores, echinoderms, mollusks, crustaceans, polychaete, bacteria and others.[1]

Harmful algal blooms (HABs) caused by toxin producing strains of phytoplankton may occur all over the world and affect all coastal areas having a strong economic impact were coastal aquaculture and tourism are important. They are known popularly as red or brown tides.

Among the macroalgae, four species have been identified as agents of world wide pest problems: *Undaria pinnatifidia*, *Codium fragile ssp. tomentosoides Caulerpa taxifolia*, and *Sargassum muticum*. *Caulerpa taxifolia* poses a serious problem in the Mediterranean and is particularly sensitive to copper sulfate and other copper compounds.

The Atlantic comb jelly *Mneniopsis leidyi* is a ctenophore that was introduced by ballast water in the Black Sea and affected seriously the ecology and fish productivity. This comb jelly has spread also into the Azov, Marmara and Mediterranean Seas Apparently, the best control of this ctenophore is the introduction of fishes that are specific predators.

The European green crab, *Carcinus maenas*, is a crustacean that causes serious damage to fisheries, aquaculture and native fauna in Eastern and Western United States, Canada, Australia, Japan and South Africa. Its control and elimination appears to be difficult.

The polychaete worm *Sabella spallanzanii*, originally from Sardinia, causes difficult problems to scallop fishers, abalone hatcheries and aquaculture in California, New Zealand and Australia.

Among the echinoderms or seastars, we mention *Asteria amurensis*, a species of the Northern Pacific that infested marine environment in Southeast Australia, mainly Tasmania. The elimination of undesired seastars in Japan, Australia, and the United States is by physical removal.[1]

Vibrio cholerae is a bacterium that is the causal agent of cholera, a disease characterized by diarrhea, vomiting and general prostration. It is transmitted through ingestion of food and beverages contaminated by feces and is predominant ia areas of poor hygiene and sanitation. This disease has killed millions of persons and continues to be a major health problem. According to well-informed sources, the seventh pandemic began in 1961 in Indonesia and spread to Africa, the Mediterranean and Eastern Europe. In 1991, ballast water from an Asian cargo ship, contaminated coastal waters mollusks and fishes in Peru and the disease spread to the rest of Latin America, affecting more than a million people and causing 10.000 deaths. Supposedly, the *Vibrio cholerae* strain responsible had been previously identified in Bangladesh. The recent cholera cases in Paranaguá, Paraná, Brazil have been traced to contaminated ballast water. Strains of *Vibrio cholerae* have been detected in Chesapeake Bay, the Gulf of Mexico, Japan and Australia.

Among the mollusks, some of environmental interest are *Corbula gibba, Crassostrea gigas, Mytilopsis sallei, Potamocorbula amurensis* and *Musculista senhousia.* Serious problems as fouling organismas are caused by three groups:
1) Mytilacea (*Mytilus edulis, Musculista senhousia, Perna ssp, Limnoperna fortun*ei,)
2) Dreissenacea (*Dreissena polymorpha, Mytilopsis sallei. Dreissena bugensis*) and
3) Corbiculoidea (*Corbicula fluminea, Corbula gibba, Potamocorbula amurensis*).

Some of these mollusks are a source of food for human consumption , poultry feed, fertilizers,while others are used as bioindicators, biofilters, pollution monitoring or cause serious biofouling, damage to water treatment installations, hydroelectric plants and aquaculture.

Perna viridis, Perna perna and Crassostrea virginica are some species that have been widely studied.

From an environmental point of view, two bivalve species are of maximum interest: the Zebra mussel (*Dreissena polymorpha*), originally from the Black Sea, that has infested almost half of the navigable waterways of the United States and the Golden Mussel (*Limnoperna fortunei*) that is becoming a grave and serious problem in Argentina, Brazil and Paraguay.[22-26]

Limnoperna fortunei (Dunker 1856) or Golden Mussel is a freshwater bivalve mussel native of Southeastern Asia. It is common in rivers and estuaries of China and its economic impact was first recorded in Hong Kong and South Korea and later in Taiwan and Japan.

In South America, its presence was first confirmed by G. Darrigan and his collaborators[16] in the River Plate in 1993. Along with *Corbicula fluminea* (Müller 1774) and *Corbicula largillierti* (Philippi 1881, the golden mussel (*Limnoperna fortunei*) is the third invading freshwater bivalve species to enter South Amereica through the River Plate (Rio de la Plata).

Its introduction is most probably due to the discharge of ballast water with high concentration of the bivalve and its larval stages by ships coming from Southeast Asia. The life of the species is similar to marine mytilids and it attaches to many hard objects, including rocks, ship hulls, wood, etc. with a byssus (an adhesion apparatus) consisting of numerous protein tethers or byssal threads.

In the subtropical region it grows rapidly, the adult reaches a length of 3-4 cm and its life span is about three years.The adults are dioic, with about two thirds of the population being female and they reproduce at least once or twice a year.[25-34]

Figure 1 shows some typical adult specimens of the golden mussel and Figure 2 gives a complete classification of the species and also shows a larval stage.

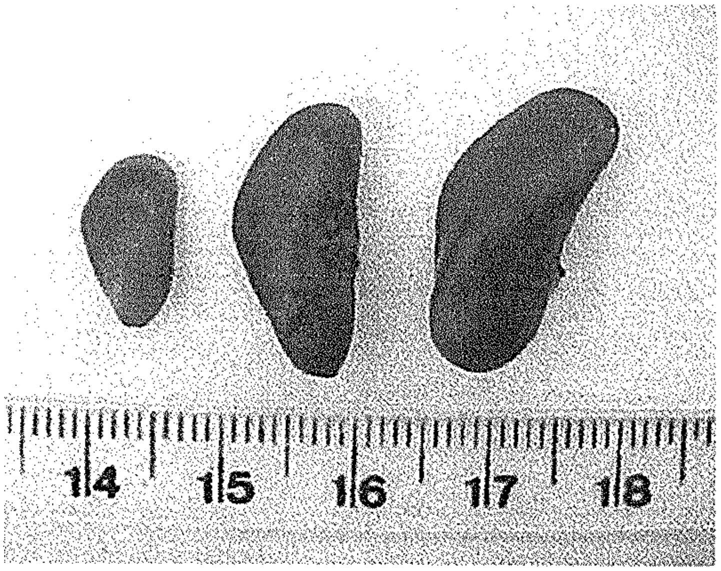
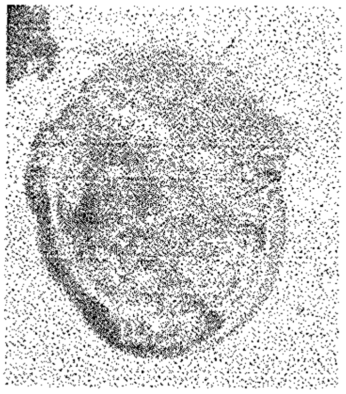


Figure1. Some Typical Adult Specimens of *Limnoperna fortunei* (Dunker 1856)[2]

Phylum: Mollusca
Class: Bivalvia
Subclass: Pteriomorpha
Order: Mytiloida
Superfamily: Mytiloidea
Family: Mytilidae
Genus: Limnoperna
Species: Limnoperna fortunei (Dunker 1856)
Common Name: Golden Mussel



a. Classification

b.Veliger larva

Figure 2. Complete Classification of the Golden Mussel, *Limnoperna fortunei* (Dunker 1856) and an example of a larval estage.

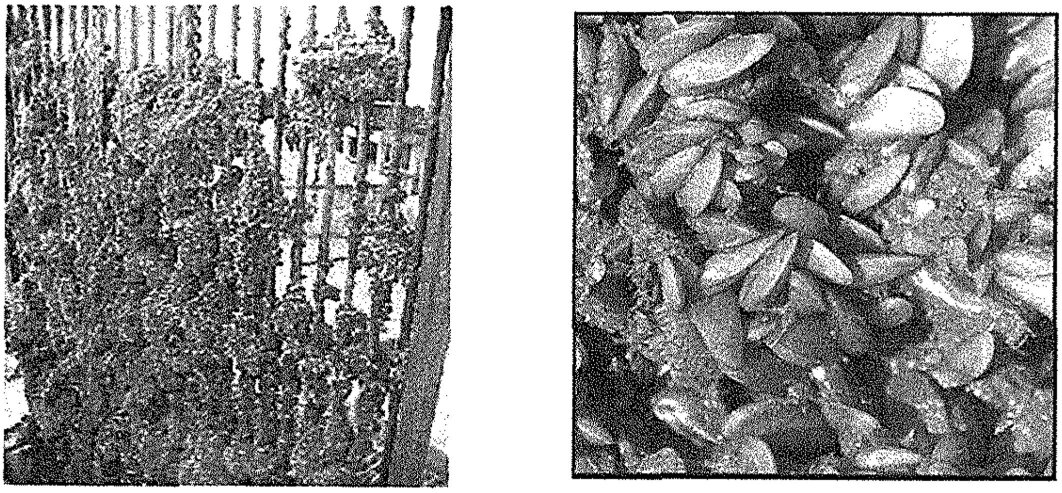
In the subtropical region, the golden mussel exhibits rapid growth, begins reproduction at an age about 30 days. It reproduces once or twice a year and has a short life span (about three years).

Its panktonic larval stage have been studied in detail[15-34]. A total of nine different larval stages have been described, five without valves and four with valves.According to C.D. Mansur and her collaborators,[7] the first one recognized as a ciliated stage develops into the trocophora (length from 80 to 125 μm) with four distinct stages. The valved stages include the D" shaped (length 120 to 150 μm), the straight hinged veliger (length 150 to 190 μm), unbonated veliger (length of 190 to 220 μm) and pediveliger (length of 220 to 250 μm)After the larval stages come the plantigrades (approximate length of 300 μm) that have a small peduncle and secrete the byssus threads that permit fixation on solid surfaces.

They attach to all kinds of hard materials, including submerged vegetation, hulls of ships, anchors, fishing equipment, parts of water distribution and irrigation systems and even other crustaceans.

Limnoperna fortunei was already considered a pest when it invaded coastal waters in South Korea and Hong Kong in the 1960's. It causes microfouling and it has a profound ecological economic and technological impact, affecting native fauna and microfauna, water supply, treatment and distribution and hydroelectric power plants.[31-34]

This species can reach densities of more tha 100,000 individuals per square meter. Figure 3 illustrtates some examples of highly dense colonies of *Limnoperna fortunei.*



(a) (b)

Figure 3. Examples of High Density Colonies of ther Golden Mussel.[2]

(a) Grating from the Water Treatment Station of Porto Alegre
(b) Turbine from the Itaipu Hydroelectric Power Plant

The high density of individuals, at times coupled with empty shell accumulation or mass mortality can cause water pipeline contamination, pipeline diameter reduction, water velocity decrease due to friction and pipeline blockage.

Serious damage and economic loss may result as far as water treatment and distribution, electric power plants, navigation docks, dams and irrigation systems are concerned.

On the other hand, the ecological and environmental impact caused by this exotic mussel, especially with regard to competition for food and living space with native species is of paramount importance.Fishing, hatcheries, oyster cultivation and other types of aquaculture activities can be seriously impaired.

The map in Figure 4 shows the extent of the spread of Limnopern fortunei (Dunker 1856) in South America. As can be seen, the golden mussel has been detected the River Plate, Paraguay, Uruguay and Paraná Rivers. Its presence has been shown also in the Lagoa dos Patos, Guaíba, Jacuí and other minor rivers .In terms of Brazil, it already covers the states of Rio Grande do Sul, Paraná, São Paulo, Mato Grosso do Sul and Mato Grosso. Hydroelectric power plants and water treatment and captation stations throughout the entire area have been affected. Even the gigantic Itaipu Hydroelectric Plant faces the infestation with the golden mussel.There is a major preoccupation that *Limnoperna fortunei* may reach the basin of the Amazon.[2]

At the present time there are no biological methods that are effective in the control of the golden mussel.

Among the physical methods[38-42] that have been tried, especially with the zebra mussel , and may be used with Limnoperna fortunei are anoxia and hypoxia (normally reducing the oxygen content in the aquatic environment) by continuous bubbling of nitrogen, ultraviolet radiation, electric or magnetic fields and acoustics. The acoustic methods involve, cavitation, sound waves, hydrodynamics and vibration. Physical methods widely used today are actual physical removal and destruction of the mussel. Of course, they imply temporary and partial shutdown of of water treatment plants and pumping stations, hydroelectric power plants and shipping docks.

Chemical methods, again have been widely studied and applied against the zebra mussel. In general the chemical compounds used are oxidizing agents with free radicals, metal ions and various types of biocides. They have been amply described in reports by the United States Army Corps of Engineers and others.[38-42] Some representative examples of chemical agents used are shown in Table I. Usually the mortality rate is very high, but other living organisms also pay a high toll.

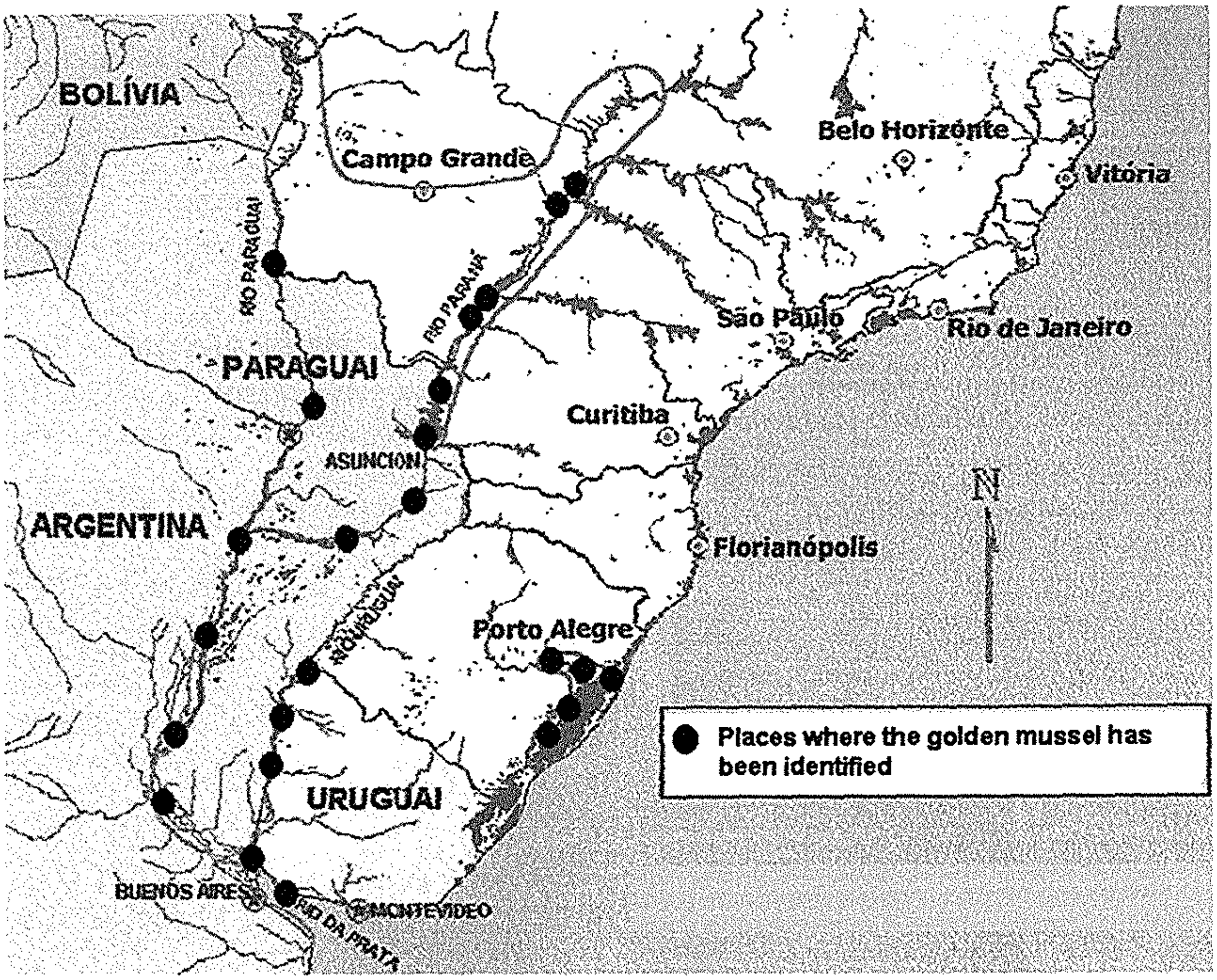


Figure 4. Occurence of the Golden Mussel, *Limnoperna fortunei* (Dunker 1856), in South America.[2]

Pratically all chemical substances may act as free radicals, alter the permeability of membranes or block enzyme action, as in the case of most metals. The physiology and toxicity of metals in different mollusks has been studied in detail.[8-15] Quaternary nitrogen compounds, that usually are also surfactants, alter the properties of biological membranes. Oxidizing agents, that include free radicals, are responsible for braking many chemical bonds and are powerful biocides.

From environmental and technological aspects, probably the most efficient methods of control are at the larval stages. They may involve actual killing of the larvae with oxidizing agents or biocides or prevention of their fixation to hard surfaces. To prevent fixation, one possibility is the use of anti-incrusting paints with tributyl tin or copper oxides or other metals. In this case, the presence of the metals as nanoparticles may be very useful.[18] Another possibility is the use of metal coated surfaces. Bioinspired antifouling materials and the mechanism of mussel adhesion[36,37] has been recently described in detail by L. Dalsin and B. Messersmith.[35]

Table I. Some Examples of Chemical Agents Used to Control Mussels.[38,41]

Chlorine	Tributyl Tin Oxide
Sodium Hypochlorite	Aluminum Sulfate
Ozone	Copper Sulfate
Chloramines	Acridine
Chlorine Dioxide	Dimethylbenzyl Ammonium Chloride
Bromine	Dodecyldimethyl Ammonium Chloride
Bromine chloride	N-Triphenyl Methylmorpholine
Sodium Bromide	Dodecylguanidine Hydrochloride
Sodium Chloride	Alkyldimethylbenzyl Ammonium Chloride
Potassium Hydroxide	Endod (Plant Extract from the Soap Berry)
Potassium Chloride	Metal Ions from Various Salts Including
Potassium Dihydrogen Phosphate	Silver, Mercury, Zinc,Lead,Copper
Dipotassium Hydrogen Phosphate	Cadmium, Tin, Gold,Chromium, Manganese
Potassium Permanganate	Commercial Molluscicides

Much more sophisticated and expensive methods involve the use of radioactive isotopes impregnated in surfaces and the use of "biobullets".[40] These are actually small food particles that contain microencapsulated highly toxic and lethal compounds. The mussels take in the "biobullets" that are later dissolved rapidly in the digestive tract and release the toxic compounds.

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