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Polymer chains interacting with a surface: Osmotic Pressure.

Georgios K.Stratouras

Kalypsous 15, Akropolis, Nicosia, Cyprus - 2014

Abstract: The interactions between polymers and the surface cause changes in osmotic pressure of the polymer solutions.

Letter to the editor.

With starting point the distribution function $G(\vec{R}_O, \vec{R}_N, N)$ of an ideal linear chain interacting with a penetrable surface[1,2], we study the osmotic pressure of the solutions of linear polymers as well as of cyclic and AB diblock copolymers interacting with a surface. As known, the realization probability of two independent events is equal to the product of the two probabilities of realization of the events apart . Thus, if the monomers of the polymers A and B of AB diblock copolymer interact with the surface via the pseudopotential of delta functions[3] $u_a\delta(z(s))$ and $u_b\delta(z(s))$ and the AB diblock copolymer is held at the point $\vec{R}_O$ where the A and B polymers are united, then the partition function for the localized AB diblock copolymer is given by the equation:

$$C_{A-B}(Z_0, U)=[1- \text{erfc}(\frac{Z_0}{2p}) +\exp\{U_a^2p^2+U_aZ_0\}\text{erfc}(U_ap+\frac{Z_0}{2p})] \times$$
$$[1- \text{erfc}(\frac{Z_0}{2q}) +\exp\{U_b^2q^2+U_bZ_0\}\text{erfc}(U_bq+\frac{Z_0}{2q})] \qquad (1)$$

where $p^2=N_a/N$, $q^2=N_b/N$ and $N=N_a+N_b$. By N_a and N_b we represent correspondingly the number of monomers of A and B polymers. Also, where $U_a=\dfrac{u_a\sqrt{6N}}{2}$ and $U_b=\dfrac{u_b\sqrt{6N}}{2}$ are the reduced interaction energies of the polymers A and B with the surface

and $Z_O = \dfrac{\sqrt{6}\,|z_0|}{\sqrt{N}\,1}$ is the reduced distance of the point $\vec{R}_O$ from the surface. Also, eq.1 describes the AB diblock copolymer interacting with a reflecting surface (unpenetrable). The integration of the eq. 1 at the point $\vec{R}_O$ gives the partition function of a free linear AB diblock copolymers interacting with a surface. Specifically when p=q, this function is,

$$C_{A-B}(U_a, U_b) = V - \frac{2\,S\,\sqrt{N}\,1}{\sqrt{6}}\; \Phi(U_a, U_b) \qquad \text{with}$$

$$\Phi(U_a, U_b) = \frac{2}{\sqrt{\pi}} - \frac{1}{2U_a} - \frac{1}{2U_b} + \frac{1}{U_a + U_b}\exp\{\tfrac{1}{2}(U_a^2 + U_b^2)\}\,\mathrm{erfc}(U_a\tfrac{\sqrt{2}}{2})\,\mathrm{erfc}(U_b\tfrac{\sqrt{2}}{2})$$

$$- \frac{U_a}{2U_b(U_a + U_b)}\exp\{\,U_b^2\}\,\mathrm{erfc}^2(U_b\tfrac{\sqrt{2}}{2}) - \frac{U_b}{2U_a(U_a + U_b)}\exp\{\,U_a^2\}\,\mathrm{erfc}^2(U_a\tfrac{\sqrt{2}}{2})$$

$$+ \frac{U_a}{U_b(U_a + U_b)}\exp\{\,U_b^2\}\,\mathrm{erfc}(U_b) + \frac{U_b}{U_a(U_a + U_b)}\exp\{U_a^2\}\,\mathrm{erfc}(U_a)] \qquad (2)$$

In the above function, V is the volume of the system and S is the area of the surface. $C_{A-B}(U_a, U_b)$ is a symmetrical function of energy. Also, for $U_a = U_b$ the above function leads to the partition function for the free linear homopolymer interacting with a plane penetrable surface. For an impenetrable surface, the corresponding partition function is given by the same type since the partition function (1) is an even function of z_O. According to the above, we are at the position to calculate the osmotic pressure. This is proportional to the derivative of the logarithm of partition function with respect to the volume of the system. Namely, for n chains this is given by the type[4],

$$\Pi = n\,\mathcal{K}T\;\frac{\partial \ln C}{\partial V} \qquad (3)$$

where $\mathcal{K}$ is the Boltzmann constant. Thus for AB diblock copolymers interacting with a surface, the osmotic pressure is given by the function,

$$\Pi_{A-B} = \frac{n\,\mathcal{K}T}{V}\;\frac{1}{1 - \dfrac{2\,\sqrt{N}\,1}{1\sqrt{6}}\Phi(U_a, U_b)} \qquad (4)$$

In eq. 4, the parameter L is defined as the ratio of the volume V over the area S of the surface. For a penetrable surface, the larger perpendicular distance on each side of the surface along which the chain can move is L/2. Also, we note that L is higher than the average length $\sqrt{N}$ l of the chain(classic limit). The eq.4, for $U_a=U_b$, leads to the corresponding osmotic pressure Π_l for the linear chain. On the other hand, for the cyclic chain, the osmotic pressure depends on the type of the surface. Thus for cyclic chain interacting with a penetrable surface the osmotic pressure is given by the function,

$$\Pi_{c,p}= \frac{n \, \mathcal{K}T}{V} \; \frac{1}{1- \frac{\sqrt{\pi N}\, l}{L\sqrt{6}}[1- \exp\{ U^2\}\operatorname{erfc}(U)]} \tag{5},$$

while in the case of an impenetrable surface the osmotic pressure is

$$\Pi_{c,r}= \frac{n \, \mathcal{K}T}{V} \; \frac{1}{1- \frac{\sqrt{\pi N}\, l}{L\sqrt{6}}[\frac{1}{2} \exp\{ U^2\}\operatorname{erfc}(U)]} \tag{6}$$

In principle, each one of the pressures, Π_l, $\Pi_{c,p}$, $\Pi_{c,r}$ and Π_{A-B} is inversely proportional to the corresponding configurational partition function. Also the partition functions are decreasing functions of the energy U; the statistical weight of the adsorbed units of the chains decreases as the monomer-surface interaction energy increases. Consequently, the osmotic pressures are increasing functions of the energy U, see fig 1, 2. Thus, in the strong adsorption limit(U→ - ∞) the osmotic pressures Π_l, $\Pi_{c,p}$ and $\Pi_{c,r}$ are zero since the whole of the chains are adsorbed on the surface. For U=0 where, then, the solution is homogenous, the osmotic pressures Π_l and $\Pi_{c,p}$ have a value equal to $\Pi= \frac{n \, \mathcal{K}T}{V}$. On the other hand, for a reflecting surface and for U=0, the osmotic pressure $\Pi_{c,r}$ has a value smaller than the above value since part of the cyclic chain is adsorbed on the surface[5] . For U→ ∞ the osmotic pressures Π_l and $\Pi_{c,p}$ obtain their maximum value which correspondingly is

$$\Pi_l= \frac{n \, \mathcal{K}T}{V} \cdot \frac{1}{1- \frac{4\sqrt{N}\, l}{L\sqrt{6\pi}}} \quad , \quad \Pi_{c,p}= \frac{n \, \mathcal{K}T}{V} \frac{1}{1- \frac{\sqrt{\pi N}\, l}{L\sqrt{6}}} \tag{7}$$

$\Pi_{c,r}$ have the same form with $\Pi_{c,p}$. Also we note that the above pressure has a slightly higher value than $\frac{n \mathcal{K}T}{V}$ since the dimensions of the system are large. Thus, we observe that the osmotic pressure changes substantially only in the case of attractions since the solution becomes poorer in monomers as the energy becomes more negative. In fig.1, the osmotic pressure, for solution of ideal linear chains, is drawn as
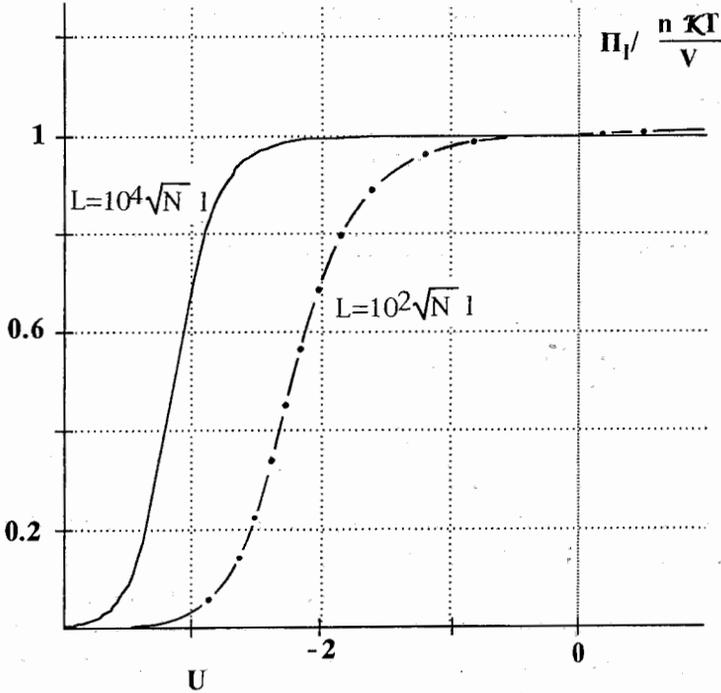
Fig 1: The reduced osmotic pressure $\Pi_l/ \frac{n \mathcal{K}T}{V}$ as a function of U for $L=10^2\sqrt{N}$ l and $L=10^4\sqrt{N}$ l

a function of the energy U for two values of L. In this figure among other observations we can see that for a given energy U the osmotic pressure becomes smaller as L increases. The more important conclusion arising from the study of the

curves $\Pi_l / \dfrac{n\,\mathcal{K}T}{V}$ - U is their S- shaped form. The steep changes near the inflection

points of the function $\Pi_l / \dfrac{n\,\mathcal{K}T}{V}$ mean that for each one L there is one critical

transition energy from the three- dimensional character of the polymer(where the longer part of the polymer lies in the solution) to the two-dimensional character of the polymer(where the longer part of the polymer is adsorbed on the surface). The above are also valid for cyclic chains. In fig.2, the osmotic pressure for the case of AB diblock copolymer is drawn as a function of energy U_a for five different values of U_b when $L=10^2\sqrt{N}$ 1 . Similarly, in this figure the curves $\Pi_{A\text{-}B} / \dfrac{n\,\mathcal{K}T}{V}$ - U_a are S- shaped.
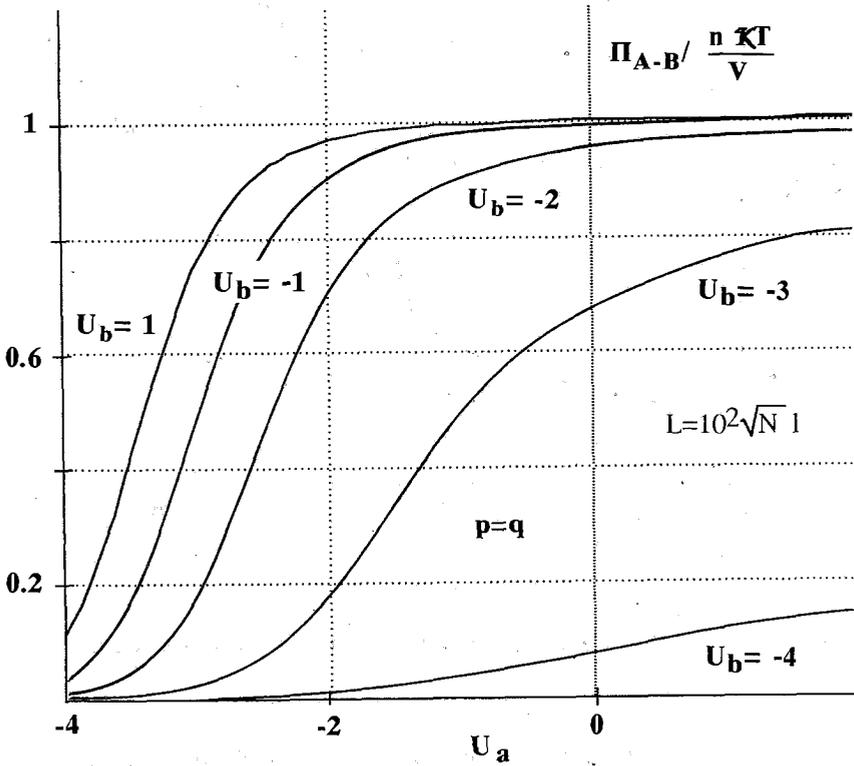
Fig 2: The reduced osmotic pressure $\Pi_{A\text{-}B} / \dfrac{n\,\mathcal{K}T}{V}$ as a function of U_a for $U_b=1,-1$, -2, -3 and -4 when $L=10^2\sqrt{N}$ 1

Moreover, in fig.2, we observe that for a given U_a(positive or not) the osmotic pressure decreases as U_b becomes more negative .

In fig. 3 the ratio of the osmotic pressures $\Pi_{c,p}$ and $\Pi_{l,p}$ is shown as a function of energy U. The pressure $\Pi_{l,p}$ is always higher than $\Pi_{c,p}$ and this is in accord with our previous results, where we saw that, under the same conditions the free cyclic chain is adsorbed more than the linear chain[6].
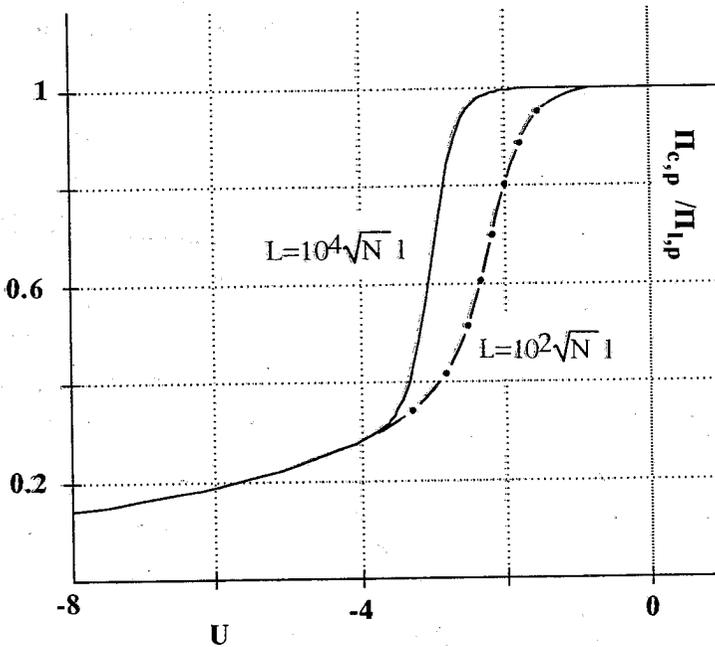
Fig 3: The ratio $\Pi_{c,p}$ / $\Pi_{l,p}$ as a function of U for $L=10^2\sqrt{N}$ 1 and $L=10^4\sqrt{N}$ 1

The osmotic pressure for ideal linear, cyclic and AB diblock copolymers (in θ conditions) interacting with a surface has been determined and studied. In conclusion, we believe that the above results seems to be suitable for experimental verification.

Περίληψη:

Πολυμερή που αλληλεπιδρούν με επιφάνεια: Ωσμωτική Πίεση.

Οι αλληλεπιδρασεις μεταξύ πολυμερών(γραμμικών, κυκλικών, AB diblock συμπολυμερών) και επιφάνειας προκαλούν μεταβολές στην ωσμωτική πίεση των διαλυμάτων των πολυμερών. Ειδικότερα στη περίπτωση των έλξεων η ωσμωτική πίεση μεταβάλεται απότομα γύρω απο την κρίσιμο ενέργεια μετάβασης του μακρομορίου απο τον τρισδιάστατο χαρακτήρα του στο δυδιάστατο χαρακτήρα του. Συγκεκριμένα, στη περίπτωση των έλξεων η ωσμωτική πίεση παίρνει τιμές απο 0 εως $\dfrac{n\,KT}{V}$. Αυτό οφείλεται στο ότι το διαλυμα γίνεται φτωχότερο σε μονομερή καθώς η ενέργεια αλληλεπίδρασης μονομερών-επιφάνειας γίνεται αρνητικότερη. Το ίδιο ισχύει και στην περίπτωση του AB diblock συμπολυμερούς που τα μονομερή του ενος εκ των δύο block του συμπολυμερούς αλληλεπιδρούν ελκτικά με την επιφάνεια. Αντίθετα, στην περίπτωση των απώσεων, ο πολλαπλασιαστικός παράγοντας που περιέχει τις αλληλεπιδράσεις είναι ελάχιστα μεγαλύτερος της μονάδας γι' αυτό και η ωσμωτική πίεση είναι ελαφρώς μεγαλύτερη απο τη τιμή $\dfrac{n\,KT}{V}$.

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KINETICS OF TEXTURE DEGRADATION IN APPLES DURING THERMAL PROCESSING

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SUMMARY

Instrumental Texture Profile Analysis can be used in studying thermal degradation of apple texture. Heating time and temperature significantly reduced fracturability, hardness, energy required during first compression and gumminess in both Red and Golden Delicious apples. Heating time did not significantly affect changes of springiness, cohesiveness and chewines in both varieties. The changes in energy required during second compression were significant for Red but not for Golden Delicious apples. Two first-order kinetic mechanisms (1 & 2) are required to describe changes of apple texture during thermal processing. The rate constant for 1 was at least 16 times that for 2; activation energy was 27.7-92.6 kJM^{-1} for both. The z values were 25-99°C and Q$_{10}$ coefficients 1.26-2.50 for both mechanisms. Such results can be used to improve thermal processes for apples.

INTRODUCTION

During heat treatment, foods undergo changes in nutrients, texture, flavour and colour; of these texture is the most apparent and the most important, especially in firm, fleshy fruits such as apples and pears[1]. The term texture is used to describe both sensory attributes and mechanical properties of food in response to applied forces, and there have been many attempts to correlate sensory and instrumental (rheological) measurements of texture[1,2,3,4,5,6]. Instrumental measurement was advanced by the General Foods Texture Profile Analysis (TPA) technique[2,7,8,9,10], in which the force-time curves yielded seven parameters, namely Fracturability, Hardness, Cohesiveness, Adhesiveness, Springiness, Gumminess and Chewiness.

As all plant species and individuals differ in chemical composition and histological structure[11], there is inherent variability and nonhomogeneity which increases the variance of instrumental measurements[12]. Holdsworth[13] has reviewed the effect of heating on fruits and Fletcher[14] reported that the variation in mechanical properties of apple slices was higher in processed than in raw fruit. Van Woensel and de Baerdemaeker[15] reported that the change of apple firmness with ripening and processing is a very complex phenomenon. Worthington and Yeatman[16] reported that firmness varies between trees, apples, varieties, type of probe, size of apple and position on apple. Bourne[17] attributed the lack of a reliable measure of apple texture to high fruit-to-fruit variability, substantial differences among seasons, moderate softening during storage and the tendency of attributes to change in different directions and at different rates.

Kinetic data on thermal degradation of food texture can be used for design of improved processes to reduce loss of all aspects of product quality. The rate of softening of various fruits and vegetables is apparently first-order[11,12,18,19,20]. Huang and Bourne[20] suggested that in several vegetables the rate of softening is consistent with two apparent first-order kinetic mechanisms, 1 and 2; mechanism 1 is probably due to pectin changes in the interlamellar spaces. The rate constants for mechanism 1 were more than 20 times greater than those of mechanism 2, and the apparent Arrhenius activation energy values ranged between 21.4 and 146.5 kJM[-1] for both mechanisms. Anantheswaran et al.[12] reported that the loss of hardness in apples followed a first-order kinetics and the activation energy was found to be 107.2 and 65.3 kJM[-1] for Cortland and Spigold varieties, respectively. They also reported z values of 24.8 and 42.4°C for the two varieties, respectively. Physical

textural characteristics were found to be a function of heating time and temperature, and apple variety[12,21,22].

The present study was undertaken to determine the effect of short and long heating times and of temperature on loss of physical texture of apples, and to verify the "apparent first-order kinetic model" for various instrumental textural parameters.

MATERIALS & METHODS

Red and Golden Delicious apples, grown in Volos area, were purchased from the Central Fruit and Vegetable Market of Athens (Greece). They were held under refrigeration (0°C, 90% RH) for a few days until processing. Only undamaged apples were manually peeled and cored and then diced into 10 mm cubes in a dicer (SOLIA-M10, France) and kept under tap water. After removal of over- and undersized pieces, the processing method of Anantheswaran et al.[12] was applied with some modifications. Apple dice (120 g) were filled into a 401x200 (103x51 mm) can followed by 240 g water at a temperature equal to that of processing or 100°C when processing temperatures greater than 100°C were used. They were then promptly sealed and placed in a preheated, thermostatically controlled water or oil bath. Temperature varied from 60-120°C, heating times from 5 to 35 min (long heating times). At the end of heating, the cans were rapidly cooled by cold (10°C) running water. The processed cans were stored at 0-2°C for 24 h and then measured. Three to 5 cans per apple variety were used for each time-temperature combination.

Huang and Bourne[20] and Anantheswaran et al.[12] observed steep initial loss in several textural parameters, mainly softening, attributed to a first-order kinetic mechanism-1. These short heating time textural changes were measured as follows: Five replicates of apple dice (20-25 g) were added to preheated (60-90°C) test tubes (50x300 mm) in a water bath and water (50 ml) at the same temperature was quickly added. At the designated time (1-15 min), sufficient ice-water was added to cool the dice, which were drained, warmed to 25°C and then force-deformation curves were measured on at least 10 dice for Texture Profile Analysis (TPA) using an Instron Universal Testing Machine model 1140 (Instron, High Wycombe, England). Fracturability (the force at the first significant break), hardness 1 (first compression), hardness 2 (second compression), springiness, cohesiveness, chewiness and gumminess were determined from the curves. Each dice was compressed twice to 80% of its original height using a crosshead and chart speed of 100 mmmin[-1].

Regression and analysis of variance were used to assess results.

RESULTS & DISCUSSION

The various textural parameters were determined from the force-time curves, which were typical of those normally obtained for apples[9,10]. Fracturability, hardness 1 and hardness 2, significantly ($p<0.001$) decreased with processing time and temperature for both varieties. The energy in Joules during the first compression (area A1) also significantly ($p<0.001$) decreased with heating time and temperature for Red and Golden Delicious apples. During second compression there was a significant ($p<0.001$) decrease in energy (area A2) with heating time and temperature for Red Delicious apples, while, for Golden Delicious apples, processing time and temperature had no significant effect. Springiness, a measure of sample elasticity, was found to change with an increase in temperature for both Red ($p<0.05$) and Golden ($p<0.01$) Delicious apples, while no significant changes occurred with changing heating time for either cultivar. Anantheswaran et al.[12] reported that in Spigold apples there were no significant changes in springiness with processing time and temperature, while in the case of Cortland significant ($p<0.05$) increases occurred with processing time. Cohesiveness was increased significantly with heating temperature for both varieties, whereas heating time had no significant effect. Anantheswaran et al.[12] found cohesiveness to change with heating temperature for Spigold and Cortland apples; heating time had no significant effect on cohesiveness for Cortland apples. Gumminess, as a product of hardness and cohesiveness, significantly ($p<0.001$) decreased with processing time and temperature for both varieties. Chewiness significantly decreased with temperature of heating for both cultivars. In Golden Delicious apples no significant changes occurred with heating time. Similar results for chewiness have been obtained by Anantheswaran et al.[12], who reported no significant changes with processing time in Spigold apples.

As it has been stated by Anantheswaran et al.[12] and showed here, textural changes in apples during thermal processing are very complex and very dependent on variety. It should be noted that there is a different behaviour of stem or root tissues and fruit tissues. The last showed larger deviation from the first-order kinetic model. Apples showed multiroute textural changes owing to the exceptionally high content of intercellular air and relative weak or thin cell walls normally occurring in apple parenchyma[11,23,24].

Semilogarithmic plots describing the change of several textural parameters showed two straight lines (Fig. 1 & 2). So, two first-order kinetic mechanisms, as proposed by Huang

and Bourne[20], can be used to describe this behaviour. To calculate the rate constants during the first few minutes of heating, the graphical procedure of Huang and Bourne[20] was followed. The linear portion obtained after prolonged heating times (mechanism 2) was extrapolated to zero heating time and the extrapolated line subtracted from the line above it (Fig. 1 & 2). The straight line obtained in this way permitted the calculation of rate constants for mechanism 1 of Huang and Bourne[20].
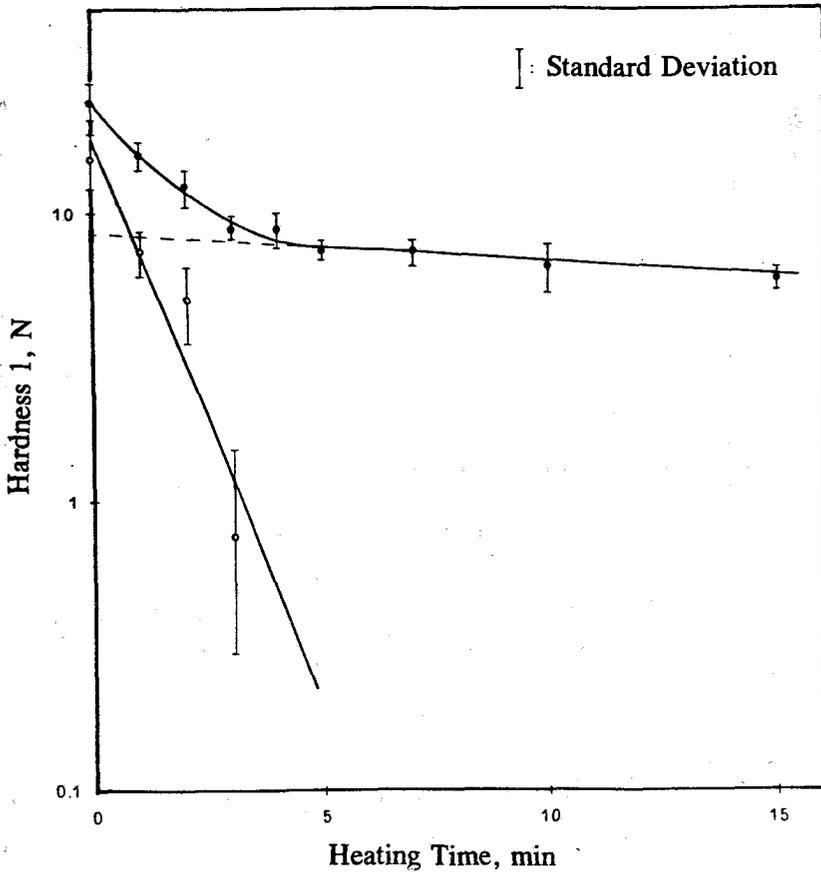
Figure 1: *Effect of heating time at 80°C on hardness of Red Delicious apples. (•) experimental points, (o) points representing differences between extrapolated line and experimental points.*
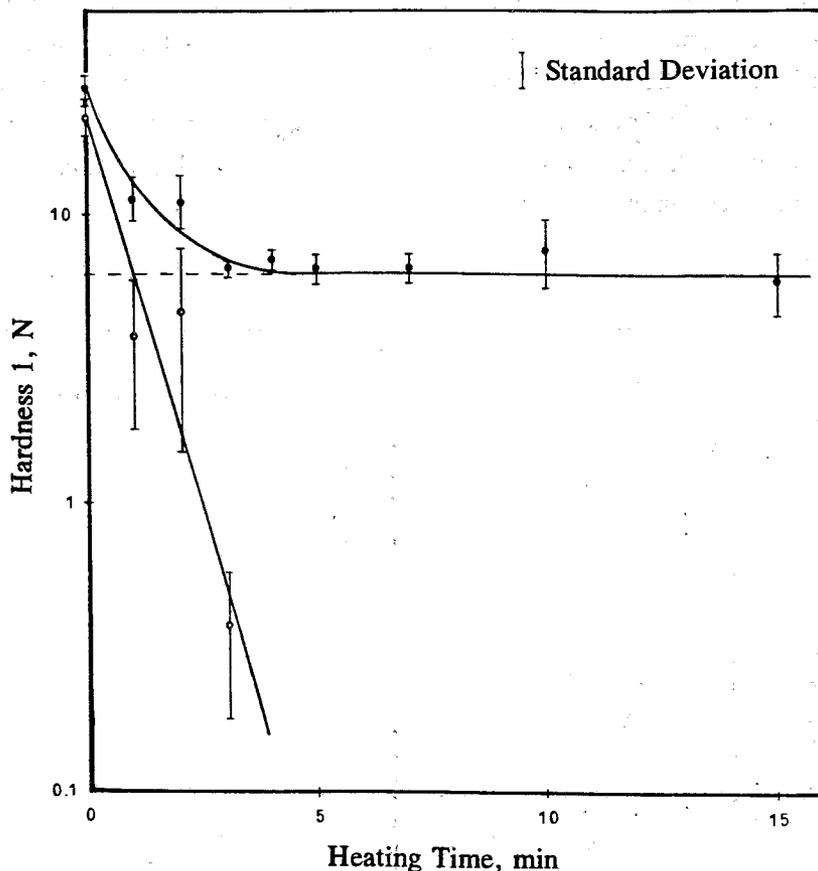
Figure 2: *Effect of heating time at 80°C on hardness of Golden Delicious apples. (•) experimental points, (o) points representing differences between extrapolated line and experimental points.*

Long Heating Times

The large drop in the magnitude of most of the textural parameters that occurred during the initial 3 min of heating, is attributed to mechanism 1[20]. Changes for heating times greater than 5 min could be attributed to mechanism 2 of Huang and Bourne[20].

The results obtained for all textural parameters were plotted vs heating time to evaluate the possibility of using the first-order kinetic model. The linear relationship between log values of fracturability, hardness 1 & 2, and heating time was significant (Table Ia & Ib) and the first-order kinetic model is adequate. Loh and Breene[11] have stated that

fracturability is the best available objective parameter for monitoring decreases in crispness of fresh vegetables during the heating process. However, problems in its measurement may arise after prolonged heating times and at high temperatures when a rather smooth graph without the peak of fracturability is obtained by Instron due to loss of crispness and high softness, as well as to inadequate load cell sensitivity of the instrument. So, the peak force representing fracturability is not easily detectable. When such a problem is faced another parameter must be used for monitoring of texture degradation. Loh and Breene[11] have used chewiness for pineapple, papaya and zucchini. Anantheswaran et al.[12] have used hardness to describe the thermal degradation of apple texture. Indeed, log of hardness 1 and hardness 2 were found to decrease linearly with heating time (Table Ia & Ib) and are adequately described by the first-order model. Hardness can always be easily measured. Hardness 2 measures the residual amount of hardness left after the first compression and is highly related to hardness 1.

Tables Ia & Ib list the decimal reduction times or D values, the rate constants (k) and the correlation coefficients (r) for various textural parameters. The D values were calculated from the slope of log(parameter) vs time curves and are included as they are more familiar to food technologists than the rate constants.

The energy required during the first compression (area A1) was modelled as a first-order process, for both varieties, and decreased with increasing temperature (Table Ia & Ib). Hence, in cases where the force for fracturability or hardness or the maximum force during the compression is difficult to measure, the area A1 (expressed in Joules or arbitrary units) could be used for monitoring of texture changes. The energy during second compression (area A2) showed a similar behaviour for Red Delicious apples, while for Golden Delicious there were no significant changes with heating time and temperature. Good correlations were obtained for temperatures higher than 80°C.

Gumminess, as a product of cohesiveness and hardness 1, is greatly affected by changes in hardness and its decrease was also modelled as a first-order process. By the same kinetics, the decrease in chewiness, can also be described, especially at high processing temperatures (Table Ia & Ib). This last parameter has been already used in monitoring textural changes in edible plant tissues[11].

Table Ia
D values (min) and rate constants, k (min⁻¹) for Red Delicious apples - long heating times.

Temp. °C	Kinetic Parameter	Fracturability	Hardness 1	Hardness 2	A1	A2	Gumminess	Chewiness
60	D	180.0±20.1	152.1±1.9	143.0±59.6	337.4±18.6	353.7±53.1	155.6±5.9	851.5±20.5
	k	0.013±0.001	0.015±0.001	0.016±0.006	0.007±0.002	0.007±0.002	0.015±0.001	0.003±0.001
	r	0.87	0.93	0.97	0.50	0.45	0.94	0.14
70	D	212.9±6.1	265.9±129.8	208.4±89.2	246.7±2.24	281.6±58.6	305.8±3.0	215.5±31.5
	k	0.011±0.001	0.009±0.004	0.011±0.004	0.009±0.001	0.008±0.002	0.008±0.001	0.011±0.002
	r	0.85	0.73	0.94	0.64	0.53	0.56	0.65
80	D	88.2±3.0	121.0±2.2	104.9±17.9	124.0±12.0	91.2±25.5	89.7±2.3	84.6±1.3
	k	0.026±0.003	0.019±0.001	0.022±0.004	0.019±0.002	0.025±0.002	0.026±0.001	0.027±0.001
	r	0.94	0.83	0.90	0.89	0.93	0.89	0.89
90	D	85.6±7.7	112.7±12.5	117.5±8.0	101.9±17.4	112.1±30.2	125.1±26.6	304.2±73.9
	k	0.027±0.002	0.020±0.002	0.020±0.001	0.023±0.004	0.021±0.005	0.018±0.004	0.008±0.002
	r	0.97	0.97	0.95	0.97	0.90	0.88	0.28
100	D	31.7±0.7	38.0±0.2	41.8±0.2	34.8±0.2	65.4±30.5	112.0±6.1	275.7±90.5
	k	0.073±0.002	0.061±0.001	0.055±0.001	0.066±0.001	0.035±0.021	0.021±0.002	0.008±0.002
	r	0.99	0.99	0.99	0.99	0.88	0.54	0.33
110	D	21.2±0.6	31.9±0.2	34.4±0.1	22.6±1.1	33.1±1.3	45.3±0.1	56.9±18.6
	k	0.109±0.003	0.072±0.001	0.067±0.001	0.102±0.005	0.070±0.003	0.051±0.001	0.040±0.014
	r	0.98	0.95	0.95	0.97	0.96	0.94	0.80
120	D	7.4±1.8	16.8±0.7	18.4±0.5	13.2±0.7	20.5±0.3	30.7±1.4	26.2±0.3
	k	0.313±0.054	0.137±0.005	0.125±0.003	0.175±0.010	0.113±0.001	0.075±0.003	0.088±0.001
	r	0.98	0.84	0.89	0.92	0.90	0.84	0.87

r=correlation coefficient, ±=standard deviation

Table Ib

D values (min) and rate constants, k (min⁻¹) for Golden Delicious apples - long heating times.

Temp. °C	Kinetic Parameter	Fracturability	Hardness 1	Hardness 2	A1	A2	Gumminess	Chewiness
60	D	313.5±55.7	275.3±238.3	297.2±70.6	241.2±67.6	694.5±75.5	146.0±19.8	90.9±16.8
	k	0.007±0.001	0.008±0.005	0.008±0.002	0.010±0.007	0.003±0.005	0.016±0.002	0.025±0.005
	r	0.66	0.89	0.85	0.85	0.14	0.81	0.89
70	D	146.2±23.1	159.6±22.0	165.3±14.0	158.6±53.8	141.3±4.6	138.6±63.5	188.1±47.2
	k	0.016±0.002	0.014±0.002	0.014±0.001	0.015±0.004	0.016±0.001	0.017±0.006	0.012±0.008
	r	0.90	0.97	0.94	0.95	0.87	0.77	0.65
80	D	177.1±112.7	304.1±207.5	276.2±34.5	40.0±25.5	605.0±32.3	196.1±180.3	189.4±10.9
	k	0.013±0.007	0.008±0.004	0.008±0.003	0.058±0.007	0.004±0.002	0.012±0.015	0.012±0.001
	r	0.66	0.57	0.52	0.62	0.20	0.36	0.17
90	D	50.0±11.5	64.5±17.3	62.7±18.7	59.7±16.4	76.8±38.7	84.8±43.9	142.2±10.4
	k	0.046±0.010	0.036±0.009	0.037±0.010	0.039±0.010	0.030±0.013	0.027±0.012	0.016±0.018
	r	0.98	0.96	0.97	0.92	0.87	0.35	0.59
100	D	19.7±2.5	28.1±0.9	30.3±0.6	24.6±0.8	34.1±2.1	44.5±3.0	44.4±13.0
	k	0.117±0.019	0.082±0.003	0.076±0.001	0.094±0.003	0.068±0.004	0.052±0.003	0.052±0.008
	r	0.98	0.97	0.97	0.96	0.96	0.93	0.86
110	D	17.0±1.0	21.7±0.5	23.2±0.7	17.8±0.7	22.3±0.3	28.6±1.4	26.1±1.1
	k	0.136±0.008	0.106±0.026	0.099±0.003	0.129±0.005	0.103±0.002	0.081±0.004	0.088±0.004
	r	0.93	0.95	0.95	0.95	0.95	0.96	0.97
120	D	15.9±0.6	20.8±0.9	22.9±1.1	16.6±0.7	27.0±3.0	40.5±6.3	37.4±8.0
	k	0.145±0.005	0.111±0.005	0.101±0.005	0.139±0.006	0.085±0.009	0.057±0.008	0.062±0.012
	r	0.94	0.95	0.94	0.95	0.95	0.92	0.93

r=correlation coefficient, ±=standard deviation

From the slope of the plot of log(D_T) vs heating temperature (Fig. 3), the z values (the degres of temperature needed for a 10 times change in D values or in time) for the change of the above textural parameters were calculated (Table II). The z values that resulted from hardness 1 were found to be 53.7 and 45.7°C for Red and Golden Delicious apples, respectively. A z value of 42.2°C has been reported[12] for Spigold apples, while a lower value of 24.8°C has been reported for Cortland apples. These differences show that apple variety is one of the dominant factors determining the changes of texture during thermal process. Using various TPA parameters a range of z values between 39-80°C was calculated (Table II).

Activation energies calculated from ln(k) vs 1/T plots for various TPA parameters were between 30.7±3.8 and 89.3±6.8 kJM[-1] (Table II). These values were within the range of 21-182 kJM[-1] reported for various fruits and vegetables[11,12,20] and dry legumes[25]. Based on hardness 1, the activation energy was 46.1±3.2 and 55.8±6.4 kJM[-1] for Red and Golden Delicious apples respectively. Higher values for activation energy have been reported for Cortland (110.95±33.08 kJM[-1]) and Spigold (65.31±15.91 kJM[-1]) apples[12]. The Q_{10} values
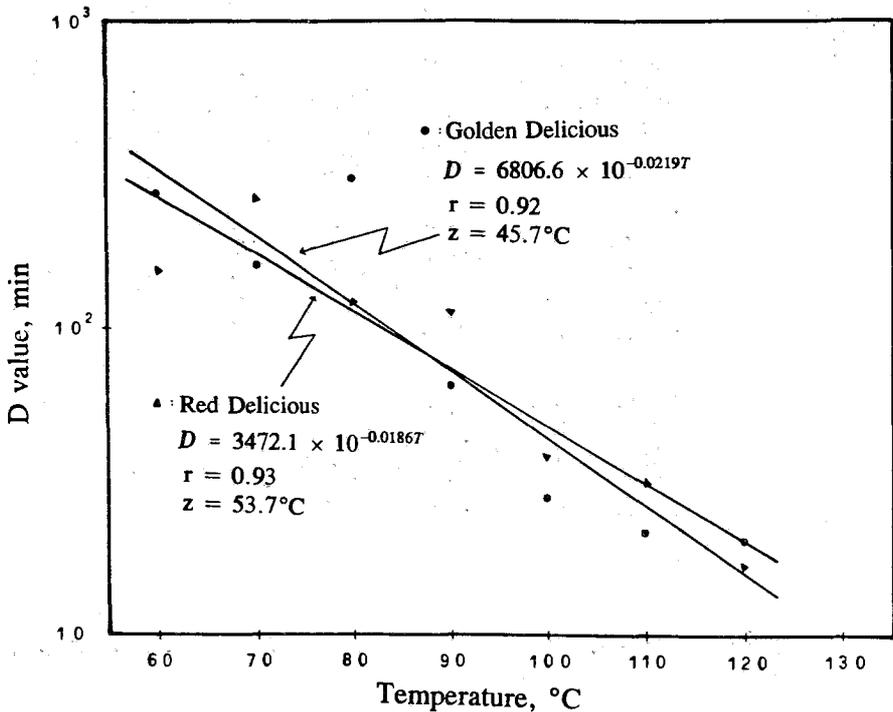
Figure 3. *Thermal degradation time curves for apple hardness*

of the microbial death are usually greater than 10. Therefore, high processing temperatures could result in a thermally processed fruit with low or minimal degradation in texture.

Table II

Temperature dependence of texture degradation rate - long heating times.

Textural Parameter	z value, °C	E_a, kJM^{-1}	Q_{10}
Red Delicious			
Fracturability	42.4±0.8(0.96)	58.6±0.9(0.95)	1.72
Hardness 1	53.7±3.5(0.93)	46.1±3.2(0.92)	1.54
Hardness 2	60.4±9.0(0.93)	41.0±6.9(0.92)	1.46
A1	41.0±3.7(0.99)	61.1±6.1(0.98)	1.75
A2	49.0±0.6(0.97)	51.1±1.3(0.97)	1.60
Gumminess	76.1±1.0(0.85)	32.4±0.6(0.84)	1.35
Chewiness	54.1±11.9(0.78)	46.1±2.8(0.77)	1.53
Golden Delicious			
Fracturability	41.7±0.6(0.95)	50.6±1.2(0.82)	1.74
Hardness 1	45.7±4.5(0.92)	55.8±6.4(0.73)	1.66
Hardness 2	46.6±0.7(0.93)	53.8±1.1(0.93)	1.64
A1	50.0±1.4(0.94)	50.6±1.1(0.95)	1.58
A2	39.5±9.5(0.88)	89.3±6.8(0.91)	1.79
Gumminess	76.0±6.1(0.88)	32.8±2.1(0.87)	1.35
Chewiness	79.9±9.8(0.76)	30.8±3.8(0.74)	1.33

±=standard deviation, in parenthesis correlation coefficient

Short Heating Times

Table IIIa & IIIb list the D values, the rate constants (k) and correlation coefficients (r) for texture degradation during short heating times. As can be seen the rate constants for mechanism 1 were more than 16 times greater than the rate for mechanism 2 (Table Ia &

Table IIIa

D values (min) and rate constants, k, (min^{-1}) for Red Delicious apples - short heating times.

Temp. °C	Kinetic Parameter	Fracturability	Hardness 1	Hardness 2	A1	A2	Gumminess	Chewiness
	D	4.2±0.1	7.2±0.8	7.3±0.6	6.7±0.7	5.8±0.5	6.7±0.2	4.8±0.2
60	k	0.55±0.01	0.32±0.04	0.31±0.03	0.35±0.04	0.40±0.03	0.34±0.01	0.48±0.02
	r	0.98	1.00	0.98	0.97	1.00	0.96	0.95
	D	2.8±0.9	4.9±0.5	2.6±0.8	2.6±0.5	2.0±0.6	2.4±0.4	2.1±0.2
70	k	0.82±0.33	0.47±0.12	0.90±0.34	0.90±0.20	1.17±0.26	0.97±0.17	1.08±0.09
	r	0.81	0.96	0.99	0.77	0.84	0.97	0.98
	D	2.4±0.5	2.5±0.0	2.1±0.0	2.3±0.4	1.4±0.4	2.0±0.2	1.7±0.2
80	k	0.96±0.20	0.94±0.02	1.12±0.02	0.99±0.19	1.71±0.54	1.18±0.10	1.32±0.15
	r	0.98	0.95	0.97	1.00	0.97	0.91	0.91
	D	1.8±0.1	1.7±0.2	1.8±0.0	2.5±0.2	1.3±0.3	1.2±0.1	1.1±0.2
90	k	1.30±0.09	1.36±0.18	1.29±0.00	0.91±1.00	1.72±0.43	1.93±0.30	2.08±0.36
	r	1.00	0.94	0.98	0.59	0.94	0.98	0.99

±=standard deviation, r=correlation coefficient

Table IIIb

D values (min) and rate constants, k, (min^{-1}) for Golden Delicious apples – short heating times.

Temp. °C	Kinetic Parameter	Fracturability	Hardness 1	Hardness 2	A1	A2	Gumminess	Chewiness
	D	3.8±0.5	17.2±6.3	14.9±5.6	5.2±0.4	6.2±1.0	20.7±0.3	10.7±3.2
60	k	0.60±0.08	0.13±0.04	0.16±0.05	0.44±0.04	0.37±0.06	0.11±0.00	0.21±0.06
	r	0.97	0.82	0.90	1.00	0.99	0.97	0.99
	D	3.7±0.1	3.9±0.2	4.1±0.0	4.6±0.7	6.1±1.3	11.8±0.7	14.6±0.8
70	k	0.62±0.01	0.59±0.03	0.56±0.00	0.50±0.07	0.38±0.08	0.20±0.01	0.16±0.01
	r	0.94	0.95	0.95	0.94	0.99	0.99	0.93
	D	2.6±0.2	1.9±0.6	2.5±0.5	2.2±0.2	2.3±0.2	2.7±0.2	1.7±0.3
80	k	0.89±0.05	1.19±0.56	0.93±0.19	1.06±0.11	0.99±0.08	0.84±0.05	1.37±0.30
	r	0.56	0.92	0.91	0.92	1.00	0.98	0.97
	D	2.0±0.9	1.0±0.1	1.5±0.1	2.1±0.3	2.2±0.2	2.6±0.2	1.1±0.1
90	k	1.15±0.54	2.45±0.11	1.50±0.14	1.11±0.17	1.03±0.10	0.90±0.08	2.06±0.10
	r	0.95	0.93	0.98	0.93	0.98	0.95	0.99

±=standard deviation, r=correlation coefficient

Ib). The z values calculated using D_T values, were between 25 and 99°C for both varieties. Based on hardness, Golden Delicious apples exhibited a lower z value than Red Delicious, showing a greater dependence on temperature, which is also evident from the greater activation energies (Table IV) and Q_{10} values of 1.3-2.5 vs 1.3-1.7 respectively. This could be attributed to differences in flesh structure between the two cultivars. Diener et al.[26] have reported that the rate of firmness decrease for Golden Delicious during maturation was about 70% higher than Red Delicious apples. So, the maturity and condition of apples can affect textural changes. Activation energies were within the range reported for various fruits and vegetables[11,12,20] and Q_{10} coefficients lower than 2.50. The change of other textural parameters, namely chewiness, gumminess, and energy during first and second compression, was also modelled as a first-order process and kinetic constants can be obtained by following the above described procedure. Values for these parameters are shown in Table IV. The change of gumminess and chewiness in Golden Delicious apples showed a greater dependence on temperature than Red Delicious apples (Table IV).

CONCLUSIONS

The above data and analysis show that textural changes in apples during the heating process are very complex and affected by variety. Heating time and temperature greatly affect most textural parameters. Heating time did not significantly affect springiness and cohesiveness in both varieties, and chewiness in Golden Delicious apples.

The rate of change of various textural characteristics was consistent with two first-order kinetic mechanisms as proposed by Huang and Bourne[20]. During the first 2 or 3 minutes of heating there was a great decrease in various textural parameters which confirmed what had been reported by Anantheswaran et al.[12]. The rate constants for mechanism 1 were at least 16 times greater than those of mechanism 2. Activation energies were between 27.7 and 92.6 kJM[-1] and Q_{10} values between 1.26 and 2.50 for both mechanisms. Q_{10} values show that the use of high temperature - short time (HTST) processes will result in a processed product of better texture. The z values for various parameters were between 25.1 and 99.0°C. The z values for loss of hardness, gumminess and chewiness due to mechanism 1 in Red Delicious apples was about twice of that in Golden Delicious apples.

Table IV

Temperature dependence of texture degradation rate - short heating times.

Textural Parameter	z value, °C	E_a, kJM^{-1}	Q_{10}
Red Delicious			
Fracturability	83.8±0.8(0.98)	27.2±0.0(0.99)	1.32
Hardness 1	45.8±6.5(0.99)	50.5±5.7(0.99)	1.65
Hardness 2	51.6±7.1(0.90)	45.4±5.6(0.91)	1.56
A1	76.2±0.9(0.78)	31.0±0.2(0.80)	1.35
A2	48.3±3.9(0.89)	48.5±5.0(0.91)	1.61
Gumminess	42.7±1.6(0.95)	60.0±2.3(0.96)	1.71
Chewiness	49.7±4.4(0.97)	46.7±4.1(0.97)	1.59
Golden Delicious			
Fracturability	99.0±3.6(0.96)	24.2±9.3(0.95)	1.26
Hardness 1	25.1±4.4(0.97)	92.7±15.5(0.98)	2.50
Hardness 2	31.5±5.9(0.96)	74.1±14.9(0.97)	2.08
A1	65.7±8.4(0.93)	35.0±4.4(0.93)	1.42
A2	57.4±5.1(0.91)	40.3±3.5(0.90)	1.49
Gumminess	29.8±0.9(0.95)	77.9±2.3(0.95)	2.16
Chewiness	25.7±2.0(0.89)	89.5±14.8(0.89)	2.45

±=standard deviation, in parenthesis correlation coefficient

Η ΚΙΝΗΤΙΚΗ ΤΗΣ ΥΠΟΒΑΘΜΙΣΗΣ ΤΗΣ ΥΦΗΣ ΤΩΝ ΜΗΛΩΝ ΚΑΤΑ ΤΗ ΘΕΡΜΙΚΗ ΕΠΕΞΕΡΓΑΣΙΑ

ΠΕΡΙΛΗΨΗ

Η ενόργανη ΤΡΑ ανάλυση μπορεί να χρησιμοποιηθεί στη μελέτη της θερμικής υποβάθμισης της υφής των μήλων. Ο χρόνος και η θερμοκρασία θέρμανσης μείωναν σημαντικά την ευθραυστότητα, τη σκληρότητα, την ενέργεια που απαιτείται κατά την

πρώτη συμπίεση και το κομμιώδες και στις δύο ποικιλίες μήλων Red και Golden
Delicious. Ο χρόνος θέρμανσης δεν επηρέαζε σημαντικά τις μεταβολές της
ελαστικότητας, συνεκτικότητας και μασητικότητας και στις δύο ποικιλίες. Οι
μεταβολές στην ενέργεια που απαιτείται κατά τη δεύτερη συμπίεση ήταν σημαντικές
για την ποικιλία Red, αλλά όχι και για την ποικιλία Golden Delicious. Απαιτούνται δε
δύο κινητικοί μηχανισμοί (1 & 2) πρώτης τάξεως για να περιγραφούν οι μεταβολές της
υφής των μήλων κατά τη θερμική επεξεργασία. Οι σταθερές ταχύτητας του μηχανισμού
1 ήταν τουλάχιστον 16 φορές εκείνης για το μηχανισμό 2. Η ενέργεια ενεργοποίησης
ήταν 27.7-92.6 kJM^{-1} και για τις δύο. Οι τιμές z ήταν 25-99°C και οι συντελεστές Q$_{10}$
1.26-2.50 και για τους δύο μηχανισμούς. Τέτοια στοιχεία μπορούν να χρησιμοποιηθούν
για τη βελτίωση των θερμικών επεξεργασιών των μήλων.

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SHORT ARTICLE

THE FORMATION AND PARTIAL CHARACTERISATION OF THE σ-BONDED PHENYL-ACRYLIC-PENTA-AQUO-CHROMIUM (III) ISOMERS: $(H_2O)_5$ CrC(COOH)=CHPh AND $(H_2O)_5$Cr(III)-C(Ph)=CHCOOH

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As part of our continuing investigation of the kinetics and mechanism of reactions of Cr^{2+} with unsaturated compounds bearing multiple bonds with polar substituents[1-4] we report herein the synthesis and characterisation of $(H_2O)_5$CrC(COOH)=CHph **(1)** and $(H_2O)_5$Cr-C(ph)=CHCOOH **(2)** whose structures conclusively support the already suggested mechanism[4] according to which the first stage of the reaction is a direct attack of Cr^{2+} on the double and/or triple bonds.

The addition of Cr^{2+} to selected olefinic double bonds has been developed to a successful synthetic method[2,5] of preparing stable organochromium (III) complexes and it was also applied[†] for the preparation of the new stable species **(1)** and **(2)** according to the equation:

$$4Cr^{2+} + 2PhC≡CCOOH +2H^+ \longrightarrow 2Cr^{3+} + [CrC(COOH) = CHPh]^{3+} +$$
$$\text{(1)}$$
$$[CrCPh = CHCOOH]^{3+} \qquad\qquad\qquad\qquad (eq.1)$$
$$\text{(2)}$$
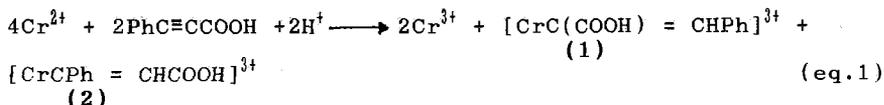
(1) and **(2)** are alkene complexes and this is the first instance in which stable organochromium cations have been prepared and

characterised from an alkynic compound. The determination of the geometric configuration of the two complexes is supported by their elution behavior and the kinetics of the Cr-C bond cleavage[6] which proceeds by slightly different rates due to an expected steric interference between the phenyl and the chromium-penta-aquo groups present at the same carbon atom in (2).

The first stage of the reaction of Cr^{2+} and phenylpropiolic acid to produce finally Cr^{3+} and phenylacrylic acid and the mechanism of this reaction are presented elsewere[4]. The formulation of (1) and (2) as σ-bonded organochromium is consistent with their spectra[1-5,7] and their decomposition products which are Cr^{3+} and trans-phenylacrylic acid in the case of their spontaneous decomposition (acidolysis)[++] and trans-phenylacrylate chromium (III) in the case of their homolytic decomposition (in the presence of Cr^{2+}).

FIG. 1 reveals the presence of Cr-C σ-bond. The bands in the UV region are attributed to LMCT (ligand-to-metal charge transfer) transitions. The spectra c, d, are the spectra of the decomposition products. Since their acidolysis product is an unsaturated compound, phenylacrylic acid, bearing a double bond, its chemical reduction with Cr^{2+} was carried out and phenylpropionic acid was obtained through formation of a σ-bonded organochromium as expected.

Especially noteworthy is the fact that by applying acidolysis conditions i.e. excess of Cr^{2+}, we are led to a homolytic

scission of the Cr-C bond due to a remote attack of Cr^{2+} on the free carboxylic group.

Further detailed studies of acidolysis and homolysis are currently underway.

+Synthesis

Solutions containing the phenyl-acrylic-penta-aquo-chromium (III) ions were prepared by injecting an amount of Cr^{2+} into an acidic solution of phenylpropiolic acid, ppa. The red complexes were isolated from the reaction mixture and purified by ion-exchange chromatography on Sephadex SP-C25 cation exchange resin. The two red distinct bands were eluted with $NaClO_4/HClO_4$ and when successive eluents showed constancy of UV/VIS spectra throughout, the isomers were collected and characterised.

++*Acidolysis conditions*[5]

The decomposition of penta-aquo-organochromium (III) complexes in aqueous solutions has been observed to occur by homolysis of the Cr-C bond (eq.2) and/or by acidolysis which may be viewed as aquation or heterolytic cleavage of the Cr-C bond with assistance from some sourse of proton (eq.3).

$$[(H_2O)_5CrR]^{2+} \longrightarrow [Cr(H_2O)_6]^{2+} + R \cdot \qquad (eq.2)$$

$$[(H_2O)_5CrR]^{2+} \xrightarrow{H^+} [Cr(H_2O)_6]^{3+} + RH \qquad (eq.3)$$
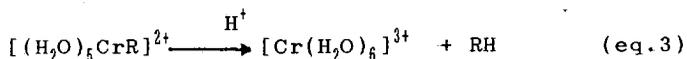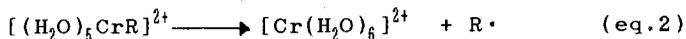
Excess of Cr^{2+} has been termed as acidolysis conditions since the
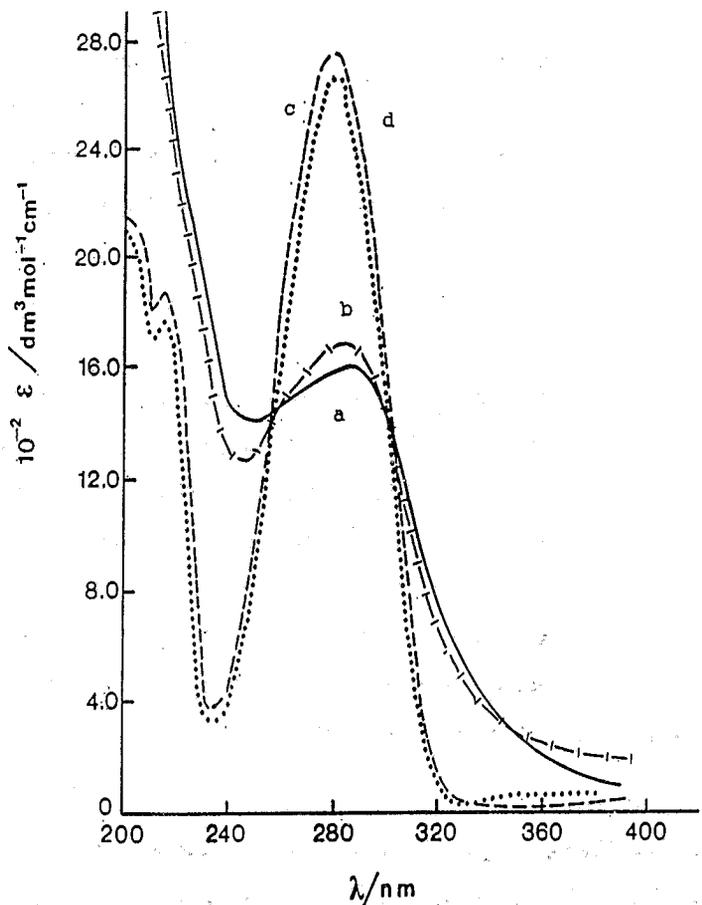
FIG.1.: *The UV spectra (a,b) of the two isomeric mononuclear organochromium complexes and spectra (c,d) of their decomposition products.*

mass law retardation effect produced by the Cr^{2+} would repress

the contribution of homolysis to the observed rate constant and

only acidolysis would then be observed.

SUMMARY

Two isomeric complexes $[(H_2O)_5CrC(COOH)=CHph]^{3+}$ (1), and $[(H_2O)_5CrC(ph)=CHCOOH]^{3+}$ (2) are formed in the reaction of $Cr^{2+}(aq)$ with $phC\equiv CCOOH$ (phenylpropiolic acid) in acidic ($HClO_4$) aqueous solutions. The complexes are isolated chromatographically and characterised by their absorption spectra and the products of their decomposition reactions (trans-phCH=CHCOOH and Cr^{3+} from acidolysis of the Cr-C σ-bond, trans-phCH=CHCOOCr and $Cr^{2+}(aq)$ from homolysis of the Cr-C σ-bond. The two complexes decompose by parallel pathways of acidolysis and homolysis.

Key words: σ-bonded organochromium complexes, acidolysis, homolysis, ligand-to-metal charge transfer bands.

ΠΕΡΙΛΗΨΗ

Σχηματισμός και μερικός χαρακτηρισμός των ισομερών συμπλόκων με σ-δεσμό Cr-C φαινυλο-ακρυλο-πεντα-υδατο-χρώμιο (III).

Δύο ισομερή σύμπλοκα τα $[(H_2O)_5-CrC(COOH)=CHph]^{3+}$ (1) και $[(H_2O)_5-CrC(ph)=CHCOOH]^{3+}$ (2) σχηματίζονται κατά την αντίδραση του $Cr^{2+}(aq)$ με το $phC\equiv CCOOH$ (φαινυλοπροπιολικό οξύ) σε όξινα ($HClO_4$) υδατικά διαλύματα. Τα σύμπλοκα απομονώνονται χρωματογραφικά και χαρακτηρίζονται μερικά με τα φάσματα απορρόφησής τους και τα προϊόντα των αντιδράσεων διάσπασής τους (trans-phCH=CHCOOH και $Cr^{3+}{}_{(aq)}$ από την όξινη υδρόλυση του σ-δεσμού Cr-C, trans-phCH = CHCOOCr και $Cr^{2+}{}_{(aq)}$ από την ομόλυση του σ-δεσμού Cr-C. Τα δύο ισομερή σύμπλοκα διασπώνται σε παράλληλες αντιδράσεις όξινης υδρόλυσης και ομόλυσης.

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PRELIMINARY COMMUNICATION

CHEMILUMINESCENCE OF NOVEL ACRIDANS

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ABSTRACT

Photolysis or radiolysis of acridine in amide solvents results in novel acridans which on addition of strong base are efficiently chemiluminescent.

We have observed that exposure of de-aerated acridine solutions in N,N'-dimethylformamide (DMF) and other amide solvents, even to the diffuse light of the laboratory, results in photolysis the same being true for γ-irradiation of said solutions in a ^{60}Co source. Subsequent addition of sodium hydride or other strong bases to the reaction mixture gives rise to intense chemiluminescence (CL).

| 1 | 2 | 3 |
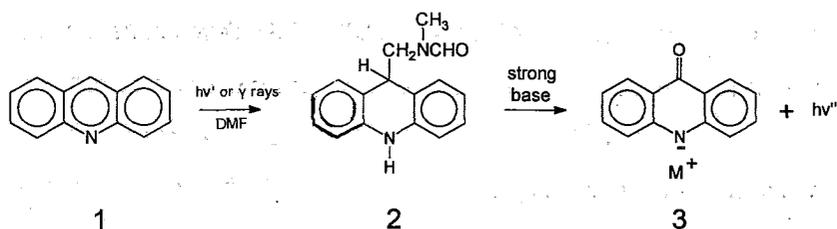
Photolysis of acridine 1 in amides has never been reported although it has been extensively studied in other solvents such as hydrocarbons, alcohols and other hydrogen atom donors[1-6]. In our experiments in DMF, photolysis with λ_{max} 357 (Oriel, Xenon lamp, 1000 watt, model 77200) results in a substituted acridan, identified[7] as 9-(N-formyl-N-methyl-aminomethyl)-acridan **2**

(Scheme), via a free radical mechanism and proton transfer from DMF with a photochemical quantum yield of over 0.32 mol . einstein^{-1}. The same product was identified and in γ-radiolysis experiments (^{60}Co Gamma chamber, 4000 A, Isotope Group, Bhaba Atomic Research Centre,Trombay Bombay, India) with radiation doses up to 1200 Gy in high yields. It should be noted here that in photolysis one expects the excited acridine, by analogy with amines[8] , to attack DMF, in contrast to radiolysis where the DMF radical[9] is expected to attack acridine. Optimum acridine concentration is 10^{-4} M, while the presence of atmospheric oxygen is deleterious to the photochemical or radiochemical reaction. Addition of sodium hydride (100 mg) to the spent reaction mixtures (1 ml, 10^{-4} M photo- or radiolyzed acridine in DMF) or the isolated acridan 2 in the dark chamber of an LKB Bioorbit luminometer resulted in CL with a quantum yield of 1.53 x 10^{-3} einstein . mol^{-1}. On employing the isolated acridan derivative 2 in DMF, the CL quantum yields was raised to 3.73 x 10^{-3} einstein.mol^{-1} . Replacement of NaH (which under said conditions is not a reductant[10]) by other strong bases such as t-buOK or MeONa resulted in quantum yields lower, yet of the same order o. magnitude.

The light reaction's CL spectrurr was identical with the fluorescence spectrum of sodium acridonyl 3, (λ_{max} 472, 498 and 531 nm) the deprotonated acridone. As isolation of this species from the spent reaction mixture was difficult, it was characterized as N-methylacridone after derivatization with methyl iodide.

In conclusion, the present system posesses the following characteristics: (a) The novel acridan derivative herein reported, readily formed and isolated, is CL with quantum yields comparable to those of the classical CL compounds such as luminol and lucigenin. (b) In contrast to the CL reactions of acridine and acridinium compounds requiring an oxidant, as with most CL reactions,

this reaction proceeds in de-aerated media in the presence of strong bases only. The oxygen required here for acridone formation comes from the solvent, but detailed mechanisms together with experimental details will be given in a full paper which is in the stage of preparation. (c) Plots of acridine absorption vs γ-irradiation dose as well as plots of CL intensity- time integrals vs γ-irradiation dose indicate that both types of plots can be employed as γ-radiation dosemeters.

ΠΕΡΙΛΗΨΗ

ΧΗΜΕΙΟΦΩΤΑΥΓΕΙΑ ΝΕΩΝ ΑΚΡΙΔΑΝΙΩΝ

Φωτόλυση η ραδιόλυση διαλυμάτων ακριδίνης **1** σε αμιδικούς διαλύτες όπως το Ν,Ν-διμεθυλοφορμαμίδιο παρέχει το υποκατεστημένο ακριδάνιο **2**. Προσθήκη ισχυρής βάσεως στο μίγμα της παραπάνω αντίδρασης δίνει ακριδόνη **3** και φως. Οι φωτονιακές αποδόσεις είναι 0.32 mol . einstein^{-1} για τη φωτόλυση και μέχρι 6.36 χ 10^{-3} einstein . mol^{-1} για τη χημειοφωταύγεια σε διμεθυλακεταμιδιο. Στην περίπτωση της ραδιόλυσης το σύστημα μπορεί να χρησιμοποιηθεί σαν δοσίμετρο γ-ακτινοβολίας.

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7 *Typical product isolation and identification of 9-(N-formyl-N-methyl-aminomethyl)-9,10-dihydroacridine 2 via radiolysis*

A solution of acridine in DMF (179 mg, 100 ml) was allowed to stand in the ^{60}Co source for 20 hrs. The solvent was evaporated to dryness in vacuo to leave a yellow solid. After washing with ether/petrolether, a pure white precipitate (158 mg, 63 %) was obtained. m.p. 176 - 178 ^0C. UV (DMF) λ_{max} 287 nm (ε=11000). Fluorescence λ_{max}, 369 nm (λ_{exc}, 287 nm). Anal. Calc. for $C_{16}H_{16}N_2O$: C 76.16; H 6.39; N 11.10. Found C 75.59; H 6.42; N 11.18. ^1H NMR (250 MHz, CDCl$_3$) δ 2.45 and 2.84 (2s, 3H, NCH$_3$, syn/anti, 1:3), 3.27 and 3.30 (2d, 2H, J=7.6/7.2 Hz, NCH$_2$, anti/syn, 3:1), 4.16 and 4.43 (2t, 1H, J=7Hz, CH, anti/syn, 3:1), 6.4 (s, 1H, NH), 6.78 (d, J=7.8 Hz, 2H), 6.93 (m, 2H), 7.07 (dd, J=7.5/1.5 Hz, 2H), 7.16 (m, 2H). ^{13}C NMR (62.5 MHz,

CDCl$_3$) δ 30.9 (C-9), 40.2 and 41.1 (NCH$_2$, syn/anti, 1:3), 51.1 and 56.4 (NCH$_3$, syn/anti, 1:3), 113.5, 113.6, 119.9, 120.8, 127.4, 127.8, 128.6, 128.7, 139.6, 162.8 and 163.0 (CHO, syn/anti, 1:3). **MS** (70 eV) m/z (%) 252 (M$^+$, 8), 193 (7), 181 (16), 180 (100, acridan), 179 (15), 85 (14), 72 (13), 59 (8), 44 (12). **IR** (KBr) 3310 (NH), 3020, 2940, 2870, 1660, 1640, 1610, 1580, 1480, 1390, 1310, 1060, 1030, 980, 880, 810, 735.

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THE SELECTIVE DETERMINATION OF METALLIC NICKEL
IN A Ni-NiO MIXTURE

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Abstract. A simple and fast method is presented for the routine control of the reduction of an NiO ore in a Ni producing plant. The metallic Ni was selectively dissolved in a AgSCN-NH4SCN solution which "extracts" Ni from the sample after its reduction. The effect of the temperature and time of treatment on the efficiency of the Ni uptake was investigated and optimized. Conditions different from these proposed in the original work of Kraft [2], were established. Determination of Ni was done applying AAS avoiding thus the step of the extraction with organic solvents neeed by the spectrophotometric method. By this way the whole precedure is 5 times faster. The method was applied for the determination of Ni in an iron-nickel sample. The same procedure is also proposed for the determination of Ni in iron-nickel ores and Co in CoO ores.

INTRODUCTION

The production efficiency of nickel in a Metallurgical plant depends on the amounts of the reduced nickel in the NiO ore, therefore it is important to have a fast analytical method to determine Ni after the sample reduction in the fluid bed furnace of the plant. The difficulty arising for the accurate determination of metallic nickel is on finding a reagent which selectively dissolves metallic nickel, or other nickel compounds. Kraft [1] recommends the AgSCN-NH4SCN reagent, which extracts only metallic nickel from a Ni-NiO mixture and the spectrophotometric determination of the Ni-concentration. This procedure is time consuming and relatively complicated, because entails a step of extraction with organic solvents.

In this presentation the same principle of extraction of the metallic nickel is used. The use though of AAS instead of spectrophotometry, makes the procedure simpler and less tedious, because it skips the extraction step. Moreover the values of the

parameters for treatment of the sample (temperature, time), proposed by Kraft, were optimized in order to make the whole procedure about 5 times faster.

The proposed procedure was also applied for the determiantion of metallic nickel in an iron-nickel ore sample, before and following its reduction in a furnace with a H_2-CO mixture in a fluid bed.

EXPERIMENTAL

Reagents and apparatus

All stock and working solutions and reagents were prepared from reagent grade chemicals.

Dissolving reagent: 120 g NH_4SCN, 40 g AgSCN, 40 g NH_4Cl and 120 g $CH_3COONa.3H_2O$ are dissolved in 800 ml distilled water, the pH is adjusted to 5 and the mixture is diluted to 1 L [1].

HCl-solution 1:1. Stock solution of HCl, 1:1 was prepared by diluting concentrated HCl-solution (10 N) with distilled water.

The NiO was prepared by heating black nickel oxide (undefined stoichiometry) at 1100 C, for 90 minute in N_2 atmosphere leading to a green product of defined stoichiometry [2].The metallic nickel is produced by reduciton of NiO with H_2.

A PYE Unicam SP-9 AAS with a deuterium background correction for the determination of nickel as used. The following instrumental parameters were applied: I=232.0 nm, ΔI=0.2 nm, H=4 nm, I=12 ma, air=5.25 l/min, C_2H_2=1.25 l/min [3].

Procedure

The effect of temperature and time on the rate of dissolution of the sample was studied using ANOVA technique [4]. During this investigation, factorial experiment design was used for a wide range of temperatures, although in this paper only one example is presented. Higher temperatures shorten the time of dissolution therefore a water bath at 100 °C was used to investigate the dissolution of the sample, in the selective dissolving reagent. Parallel experiments were performed using 1:1 HCl as dissolving reagent and the same amounts of sample as those used for the selective dissolution. This procedure brings the total amount of the nickel (Ni+NiO) into solution.

For each working temprature, the amount of the uptake of Ni from the NiO standard sample (green product) was determined.

The following procedure of treatment of the sample was applied: The pulverized sample was shaken in a 50 ml flask with 30 ml of the extracting reagent, at a defined temperature and time. The solution was set to cool, and from the supernatant solution a known volume was transfered to a volumetric flask (the volule of the flask depends

on the degree of uptake). If the solution does not need any dilution it was directly introduced in the flame of the AAS. The flask was filled to the mark with NH_4SCN solution (50 g/l).

The effect of two parameters were investigated each at three different levels, applying ANOVA technique:

Time : 60 min, 90 min and 120 min.

Temp: 25 °C, 35 °C and 45 °C.

For each combination of experimental conditions samples were analysed in triplicate.

RESULTS AND DISCUSSION

The factorial experiment is carried out on metallic nickel, ground with a mortar and pestle. The metallic nickel was obtained by reduction of NiO in the laboratory. Results are shown in Table 1. In his paper Kraft [1] recommended 36 °C and 120 min as optimal values for temperature and time of treatment. Moreover he stated that increasing the temperature up to 50 °C no effect was observed on the uptake of Ni. In fact, in this work it was proved that by increasing the temperature, the dissolving time is shortened. According to experimental results not shown here this trend continues also for temperatute higher than 40 °C. The dissolving time of metallic nickel is reduced to about 20 minutes by 100 °C working temperature. The effect of temperature and time as well as their interaction shows a profound correlation with the uptake of Ni. From Table 1 it was also concluded that nickel obtained by reduction is totally in its reduced form (experiments Nr. 1,2,5 and 10). Table 2 shows results taken for 100 °C at three different dissolving times.

Paralell experiments have shown that at 100 °C the amount of nickel dissolved form 100 mg NiO (green) was only 0.23 mg, almost negligible.

This procedure was also applied in determining metallic nickel in the nickel iron ore, which is a usual raw material in Metallurgical Combines. The determination is carried out before and after reduction of the ore in fluid bed of a plant's furnace. The concentrations of some elements in two samples (before and after reduction) are shown on table 3. Using the proposed selective procedure for metallic nickel determination on the above samples, it was found that the content of metallic nickel after reduciton of the ore was increased to 78 % of the total nickel in the sample (the rest remained in its oxide forms). The values were calculated after background correction.

The same procedure was also successfully applied in the determination of metallic Co in CoO ores.

Table 1. Experimental results showing the effect of temperature and time on the uptake on the uptake of Ni.

| Nr | Time, min | Temp. ºC | Absorbance | | |
			Run 1	Run 2	Run 3
1	120	45	0.066	0.067	0.064
2	120	35	0.065	0.064	0.066
3	60	35	0.050	0.041	0.047
4	60	45	0.059	0.060	0.061
5	90	45	0.067	0.064	0.066
6	90	35	0.056	0.055	0.057
7	60	25	0.035	0.038	0.032
8	120	25	0.055	0.051	0.058
9	+90	25	0.054	0.053	0.057
10*			0.067	0.066	0.065

*The experiment Nr 10 was performed in HCl (1:1).

Table 2. The vlaues of absorbances at 100 ºC for 20, 30 and 45 minutes.

Time min	Run 1	Run 2	Run 3
20	0.068	0.067	0.069
30	0.067	0.068	0.066
45	0.066	0.068	0.069

Table 3. Total % concentration of Ni, Co and Fe in an iron-nickel ore after complete dissolution in HCl-solution.

	Ni %	Co %	Fe %
After reduction	1.08	0.068	55.64
Before redution	0.97	0.061	52.89

Conclusions

The proposed procedure for the determination of metallic nickel can be applied successfully using an AS technique. The optimal temperature to dissolve the sample is at 100 °C on water bath reducing thus the analysis time 5-6 times compared to the procedure of Kraft [1]. This procedure may be also applied routinely to control the level of reduction of nickel in iron-nickel ores in a furnace of a metallurgical plant.

ΠΕΡΙΛΗΨΗ

Περιγράφεται απλή και ταχεία μέθοδος για τον έλεγχο ρουτίνας αναγωγής με- ταλλεύματος NiO σε εγκαταστάσεις παραγωγής νικελίου. Το μετάλλευμα νικελίου διαλύεται εκλεκτικά σε διάλυμα AgSCN-NH₄SCN, το οποίο «εκχυλίζει» το νικέλιο από το δείγμα μετά την αναγωγή. Μελετήθηκαν και βελτιστοποιήθηκαν η θερμοκρασία και ο χρόνος επεξεργασίας για την αποδοτικότερη παραλαβή του νικελίου. Καθορίστη- καν διαφορετικές συνθήκες από τις προτεινόμενες στη βασική εργασία του Kraft. Ο προσδιορισμός του νικελίου έγινε με φασματομετρία ατομικής απορρόφησης, απο- φεύγοντας έτσι το στάδιο της εκχύλισης με οργανικούς διαλύτες που περιλαμβάνει η χρησιμοποιούμενη φασματομετρική μέθοδος. Με τον τρόπο αυτό, η όλη διαδικασία γίνεται πέντε φορές ταχύτερα. Η μέθοδος εφαρμόσθηκε στον προσδιορισμό νικελίου σε δείγμα σιδήρου-νικελίου. Όμοια διαδικασία προτείνεται για τον προσδιορισμό νι- κελίου σε μεταλλεύματα σιδήρου-νικελίου και κοβαλτίου σε μεταλλεύματα CoO.

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CHIMIKA CHRONIKA, *NEW SERIES*

CONTENTS