

## Uptake of $\text{Cu}^{2+}$ by Starch Granules As Affected by Counterions

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Potato and wheat starch granules were soaked in 1% aqueous solutions of copper(II) salts: acetate, chloride, and sulfate. Such treatment caused sorption of  $\text{Cu}^{2+}$  ions at the granule surface and their penetration into the granule interior as was proven, for sectioned granules of investigated starch, by scanning electron microscopy combined with an X-ray microanalysis system (energy dispersive spectroscopy). Copper ions incorporated into the granules influenced the starch thermal stability. Uptake of  $\text{Cu}^{2+}$  by potato, determined by flame atomic absorption spectrometry, was much higher than obtained for the wheat starch. Moreover, it was dependent on copper counteranions present in the solution. In all investigated granules, the most effective sorption occurred in the acetate solution. Starch dehydration or/and freezing and thawing, affecting the water-dependent inner structure of the granules, also influenced the amount of  $\text{Cu}^{2+}$  taken from the solutions. Thus, compared to that in native starch, this value was considerably higher in  $\text{Cu}(\text{CH}_3\text{COO})_2$ , almost unchanged in  $\text{CuSO}_4$ , and significantly lower in the case of  $\text{CuCl}_2$  solution. The influence of chloride and sulfate anions seemed to correlate with their water structure-making and structure-breaking ability, affecting the migration of  $\text{Cu}^{2+}$  in the amorphous parts of the granules. However, high Cu uptake observed for acetate solution could be explained on the basis of acetate anion hydrolysis activating the polysaccharide matrix for cation binding. The obtained results provide new information about interactions of starch granules with salt solution and therefore support our understanding of starch properties.

**KEYWORDS:**  $\text{Cu}^{2+}$  distribution in starch; anions in starch granules; starch–electrolyte interactions

### INTRODUCTION

Starch is a widely available raw material used in the food industry and in many other technological applications. This carbohydrate polymer, composed of glucose units, consists of two fractions: linear amylose and branched amylopectin. It was already shown that starch granules soaked in salt solutions can retain cations of alkali and transition metals, presumably in the form of starch–metal complexes (1–5). Potential sites of such linkage are the hydroxyl groups of each glucose unit as well as the oxygen atoms of either the pyranose ring or glycosidic bonds (6). In potato starch, the phosphoric acid moieties, bound to the carbohydrate chains, make this starch anionic and enhance its natural cation-exchange properties (7, 8).

Copper is an essential trace nutrient which performs a number of diverse functions in protein biochemistry. Its compounds,

including copper acetate, sulfate, and chloride, investigated in the present work, are utilized for agricultural purposes as pesticides (fungicides and herbicides) and feed and soil additives. Higher exposure of living organisms to copper salts may cause systemic toxic effects, so they are designated as hazardous substances for the natural environment. Binding of metal ions to polysaccharides may influence, via a food chain, the distribution of minerals in living organisms. Therefore, this could be useful for provision of the daily diet and/or removal of harmful minerals from the organisms. The process could also be applied for separation and recovery of copper ions in environmental samples, e.g., from highly concentrated production effluents (9, 10).

Numerous studies on starch interactions with metal salt solutions resulted in ambiguous conclusions. Some authors stated that starch could absorb entire salt molecules (3, 11); others presented an opinion that only anions could be taken by the granules while cations were localized at the granule surface (12). It was also postulated that hydrated cations could freely penetrate the granules (1, 13, 14), but their localization at the granule surface or in the granule interior was not substantiated by the experimental data. According to several other papers,

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**Table 1.** Uptake of Cu<sup>2+</sup> by Starch Granules from Studied Salt Solutions<sup>a</sup>

starch sample		amt of Cu (mg) per 1 g of starch		
		Cu(CH <sub>3</sub> COO) <sub>2</sub> salt solution	CuCl <sub>2</sub> salt solution	CuSO <sub>4</sub> salt solution
potato	native	1.61 (0.03)	1.47 (0.17)	0.83 (0.01)
	dried	1.97 (0.01)	0.86 (0.01)	0.84 (0.01)
	dried and frozen/ thawed without water	2.75 (0.04)	0.98 (0.03)	0.96 (0.02)
	dried and frozen/thawed in water suspension <sup>b</sup>	1.63 (0.03)	0.73 (0.03)	nd
wheat	native	0.62 (0.02)	0.24 (0.09)	nd
	dried and frozen/ thawed without water	1.13 (0.03)	nd	nd
	dried and frozen/thawed in water suspension <sup>b</sup>	0.61 (0.02)	0.12 (0.02)	nd

<sup>a</sup> Samples were prepared and analyzed in duplicate. Standard deviations are given in parentheses. nd = not determined. <sup>b</sup> Starch:water = 1:1 (v/v), frozen/thawed in five cycles.

anions could enter the granules and then, in favorable circumstances, act as gelatinizing agents by rupturing the hydrogen bonds between the starch molecules (14, 15). In light of the previous study, the starch–metal salt interactions are affected by many factors, such as the Donnan potential between starch and the water phase, behavior of salt ions in aqueous solution, and free water content of the granules. However, neither the latter factor nor the influence of the counterions on the metal ion uptake by starch was quantitatively investigated. The present study was undertaken for solutions of various copper salts to determine the effect of accompanying anions on the metal cation sorption occurring in potato and wheat starch granules. Moreover, the possible localization of the absorbed Cu<sup>2+</sup> in the granules was investigated.

## MATERIALS AND METHODS

**Materials.** Two kinds of commercially available starch were used in the investigations: potato starch isolated according to ref 16 and wheat starch (Kröner Stärke GmbH & Co., Ibbenburen, Germany).

**Sample Preparation.** In the experiments starch was used as ambient native starch or after 3 h of drying in an oven at 120 °C (19% and 7–8% moisture for native potato and wheat starch, respectively). The applied oven-drying did not induce the B-type to A-type transition in the starch granules as was checked by X-ray diffraction (17). Dried starch was also frozen in liquid nitrogen without water or in an aqueous suspension (starch:water = 1:1, v/v) as was described elsewhere (18). Samples (about 10 g) of granular native or modified starches were agitated with constant shaking in 130 cm<sup>3</sup> of 1% aqueous solutions of the appropriate copper(II) salts, i.e. CuCl<sub>2</sub>, Cu(CH<sub>3</sub>COO)<sub>2</sub>, and CuSO<sub>4</sub> (POCh, Poland) for 24 h at 40 °C. Afterward, the samples were filtered off, washed three times with water and next with ethanol (99.8%, POCh), centrifuged, and dried in a dryer at 50 °C. Ethanol facilitated drying of starch and was completely evaporated before further measurements.

**Atomic Absorption Spectrometry (AAS).** The total copper content in the samples, after their wet mineralization with HNO<sub>3</sub>, was determined by using the Solaar M6 spectrometer (THERMO Scientific) and a standard procedure of AAS (19). The samples were prepared and analyzed in duplicate.

**Scanning Electron Microscopy–X-ray Microanalysis (Energy Dispersive Spectroscopy) (SEM–EDS).** Starch granules, after treatment with Cu salt followed by drying, were mixed with the rapid-setting epoxy resin Poxipol (Akapol SACIFA). The mixture was transferred to a mold and air hardened for 24 h. After this, the granules were cut across using a glass knife microtome. The freshly sectioned granules were air-dried and covered with a thin layer of graphite. Qualitative mapping of both the surface of the granules and their interior was performed with the scanning electron microscope Philips XL 30 (FEI Philips Electron Optics) operated at 20 keV, equipped with an energy dispersive X-ray spectroscope, Link ISIS EDS system (Oxford Instruments Ltd., U.K.). The samples were prepared in duplicate; images of the surface and the interior of the several starch granules were collected. The SEM–EDS signals obtained for the granules soaked in copper chloride and copper sulfate solutions were not sufficiently high for qualitative analysis with the method used.

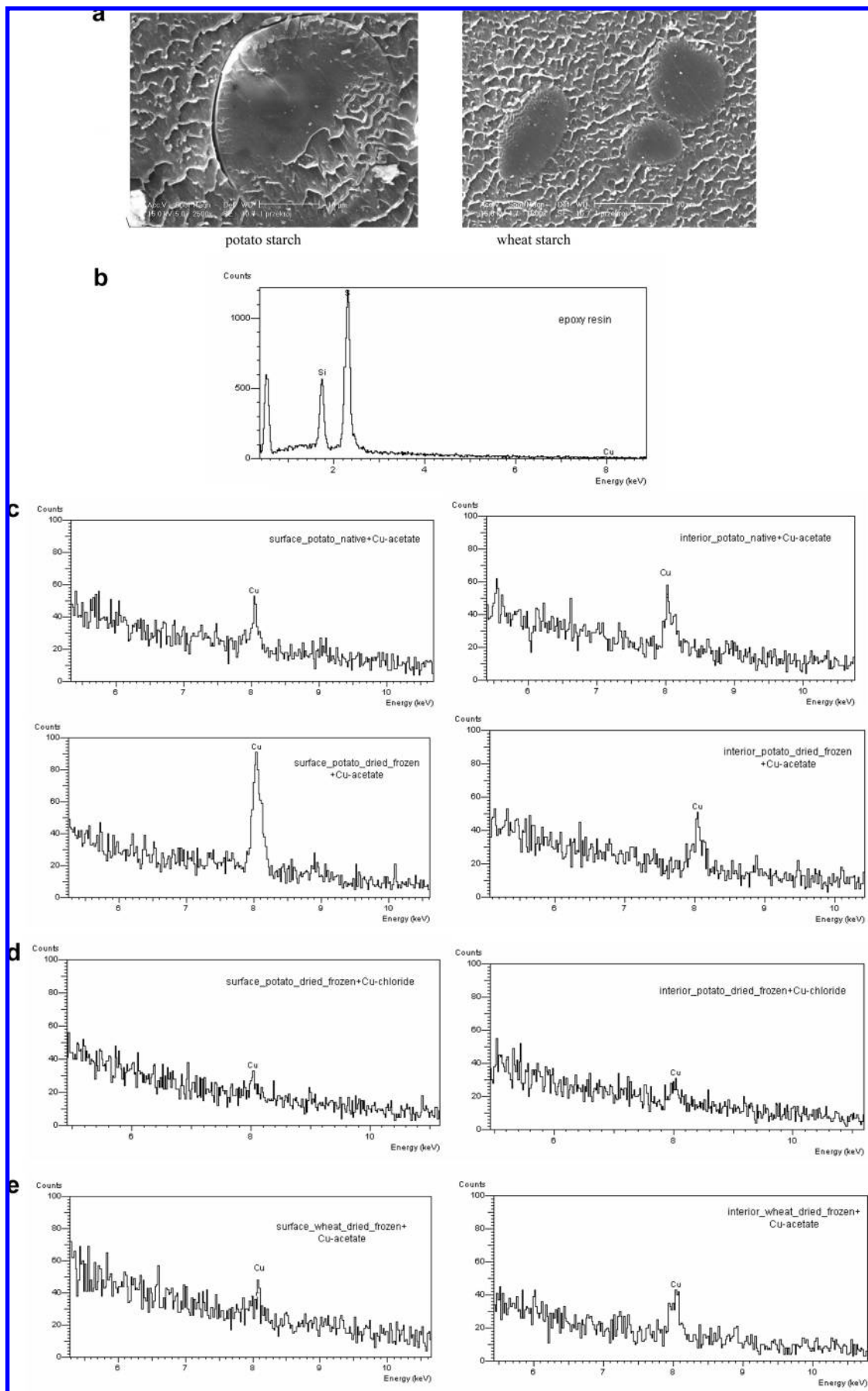
**Thermal Analysis (DSC, EGA-TG/DTG/SDTA).** Differential scanning calorimetry (DSC) measurements were carried out using a Mettler-Toledo 821<sup>c</sup> calorimeter equipped with a Haake intracooler under a flow of argon (80 mL/min) within the temperature range of 25–600 °C at a heating rate equal to 5 °C/min. The starch samples of 5–10 mg were investigated in 40 μL aluminum crucibles closed by a lid with a hole of 1 mm diameter.

Thermal gravimetry analysis (TG) coupled with simultaneous differential thermal analysis (SDTA) was carried out in the Mettler-Toledo 851<sup>c</sup> thermoanalyzer using 150 μL corundum crucibles under a flow of argon (80 mL/min), within the temperature range of 30–600 °C at a heating rate of 5 °C/min. The simultaneous analysis of the evolved gas by mass spectrometry (EGA-MS) was realized by using an online joined quadruple mass spectrometer (QMS) (Thermostar-Balzers Instruments). The TG and DSC measurements were calibrated by a standard procedure of the Mettler-Toledo Star<sup>c</sup> software with melting of pure indium as a reference.

## RESULTS AND DISCUSSION

AAS measurements indicated that sorption of the Cu<sup>2+</sup> ions occurred in both kinds of the investigated granules, i.e., potato and wheat starch (Table 1). Copper was selectively detected, with the use of the SEM–EDS method, not only at the surface but also in the interior of the potato and wheat granules, which were cross-sectioned after having been soaked in copper acetate solution (Figure 1). This provided experimental evidence of penetration of the Cu<sup>2+</sup> into the starch granules. It should be noted that the CH<sub>3</sub>COO<sup>−</sup> ions could not be detected by the EDS method. The SEM–EDS signals obtained for the granules soaked in CuCl<sub>2</sub> and CuSO<sub>4</sub> solutions, due to the low amount of copper ions, were not sufficiently high for the qualitative evaluation with this method.

Uptake of Cu<sup>2+</sup> by potato was much higher compared to that by the wheat starch. Such an effect was previously noticed by one of us (J.Sz.) for CuCl<sub>2</sub> solution (20). It was probably caused by the large size of the potato starch granules and their B-type crystalline structure as well as by the presence in potato of phosphate groups influencing the granular water content and the starch swelling ability (8, 21). The amount of copper ions bound to the granules was found to be dependent on the counteranions present in the solution. In all investigated starch samples the most effective sorption occurred when Cu<sup>2+</sup> ions were accompanied by acetate ions (Table 1). This pointed to the penetration of anions, together with cations, into the starch granules as was suggested previously (14, 15). We observed that dehydration and freezing/thawing of starch also influenced the amount of copper taken by the granules from the investigated salt solutions. Compared to that in native starch, the effect was found to be considerably higher in Cu(CH<sub>3</sub>COO)<sub>2</sub>, almost unchanged for CuSO<sub>4</sub>, and significantly lower in the case of CuCl<sub>2</sub> solution. This indicated that the granule inner microstructure, depending on the starch moisture content, played an



**Figure 1.** SEM images of the cross-sectioned granules soaked in  $\text{Cu}(\text{CH}_3\text{COO})_2$  solution (**a**) and EDS spectra: (**b**) epoxy resin background, (**c**) potato starch +  $\text{Cu}(\text{CH}_3\text{COO})_2$ , (**d**) potato starch +  $\text{CuCl}_2$ , (**e**) wheat starch +  $\text{Cu}(\text{CH}_3\text{COO})_2$ .

**Table 2.** DSC Parameters of Potato Starch Sample Decomposition

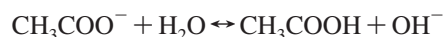
potato starch sample	water evaporation		decomposition				water content by DSC <sup>a</sup> (%)	TG decomposition (%)
	T <sub>max</sub> (°C) ± 0.1	ΔH (kJ mol <sup>-1</sup> )	onset A T (°C) ± 0.1	ΔH <sub>A</sub> [J g <sup>-1</sup> ]	onset B T (°C)	ΔH <sub>B</sub> (J g <sup>-1</sup> )		
native	85.6	-51.05	258.6	-135.9	325.5	11.5	11.62	76.54
native + copper acetate	81.7	-50.65	235.4	-167.9	306.1	115.6	11.35	69.52
dried	91.2	-52.31	259.7	-137.0	327.2	11.0	4.20	77.50
dried + copper acetate	102.2	-55.61	234.8	-123.5	304.0	57.7	12.23	69.74

<sup>a</sup> Calculated for ΔH<sub>vap</sub>(H<sub>2</sub>O) = -2834 J g<sup>-1</sup> = -51.0 kJ mol<sup>-1</sup>.

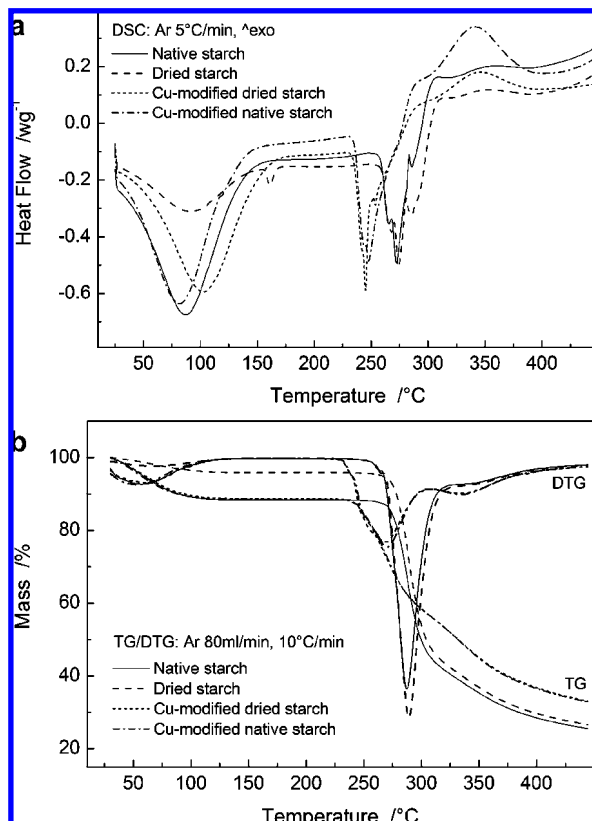
important role in the studied Cu<sup>2+</sup> sorption. Copper ions were introduced to starch granules in the form of hexaaqua complexes [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> typical for aqueous solutions of copper salts used for starch soaking. As was already shown, the cations could be accumulated by starch due to interactions with granular water molecules (that is, as the [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> species) as well as with the oxygen atoms of the glucose hydroxyl groups and/or the phosphate monoesters present in the granules (20). Such Cu<sup>2+</sup>-starch complexes were formed by substitution of water molecules in the coordination sphere of [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> by oxygen atoms of the carbohydrate matrix. In [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, however, the copper ions coordinate water molecules from the amorphous parts of the granules, i.e., the amorphous growth rings and amorphous lamellae of the semicrystalline growth rings. In a sufficient amount of water, e.g., in native starch granules, such species could migrate through the granule amorphous regions, enhancing the cation accumulation and binding by the starch matrix. Decreasing the granular moisture content resulted in disruption of the granule microstructure. Therefore, dehydration or/and freezing/thawing of starch should change the efficiency of Cu<sup>2+</sup> sorption in disordered amorphous parts of the granules. Indeed, this was observed in our study for CuCl<sub>2</sub>. Drying of starch at 120 °C, removing water from the amorphous growth rings as well as the amorphous lamellae of the semicrystalline growth rings of the starch granules, significantly decreased the amount of Cu<sup>2+</sup> taken by the granules from chloride solution. It could be therefore concluded that, in this case, copper ions might be coordinated to both the granule amorphous and crystalline regions. This is in accordance with the results obtained by one of us by the EPR method (20). Quite the contrary, in CuSO<sub>4</sub> solution, drying did not influence the copper sorption. This indicated preferential binding of the Cu ions to the crystalline parts of the polysaccharide matrix in the presence of SO<sub>4</sub><sup>2-</sup>, as was already postulated in some papers (4, 6). The influence of chloride and sulfate anions on Cu<sup>2+</sup> sorption in starch seemed to correlate with their position in the lyotropic (Hofmeister) series. On the basis of the liquid water structure model, ions behave in aqueous solution depending on their size and charge density (22). Anions are more strongly hydrated (they more strongly bind water molecules compared to the strength of water-water interactions in bulk solutions) than cations for a given charge density (15, 23). Ions of high charge density, such as SO<sub>4</sub><sup>2-</sup>, exhibited strong electrostatic interactions with water molecules (strongly hydrated "structure makers", the standard ionic enthalpy in aqueous solution ΔH<sub>sol</sub> = -907.5 kJ mol<sup>-1</sup> (24)) and reduced the free water fraction available for cation hydration in the granules. In such circumstances, the limited migration of Cu ions (as the [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> species) through the amorphous regions, even in native starch granules, might result in favorable coordination of Cu<sup>2+</sup> to the starch crystalline regions. Chloride ions, having low charge density (weakly hydrated "structure breakers", ΔH<sub>sol</sub> = -167.4 kJ mol<sup>-1</sup> (24)), caused breaking or weakening of hydrogen bonds

between water molecules and increased the fraction of free water capable of hydrating the copper ions in the amorphous parts of the granules. In native starch granules, this supported migration of the Cu<sup>2+</sup> ions and their retention in the polysaccharide matrix. It was found, moreover, that dried granules bound the same amount of Cu<sup>2+</sup> in both the chloride and sulfate solutions. This amount might be assumed as an equilibrium quantity of copper cations attracted, in the studied conditions, by the active groups of the starch crystalline regions. Starch dehydration and freezing/thawing significantly increased the specific surface area and porosity of the granules (18), which should enhance sorption via the granule surface. In our study, this effect was probably compensated by simultaneous higher, compared to that in the native starch, leakage of the granule amorphous moiety during the salt solution treatment (21). Thus, only a slight increase in Cu<sup>2+</sup> uptake was observed for thermally modified granules soaked in CuCl<sub>2</sub> and CuSO<sub>4</sub>.

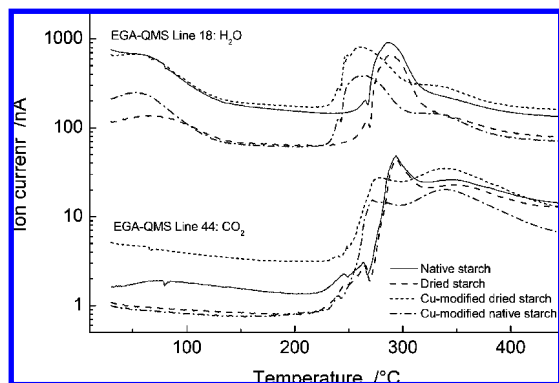
Uptake of copper ions from acetate solution was much higher than obtained for the other investigated solutions. This could hardly be rationalized on the basis of the position of acetate ion in the Hofmeister series (intermediate compared to Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, ΔH<sub>sol</sub> = -491.6 kJ mol<sup>-1</sup> (24)) only. In this case, the anionic hydrolysis occurring in the aqueous solution should be considered as a factor enhancing coordination of Cu<sup>2+</sup> to the starch matrix. The latter reaction, according to the scheme



providing the system with an additional amount of OH<sup>-</sup>, slightly increased the pH value of copper acetate solution compared to the other solutions under study. This might be sufficient for local activation of the polysaccharide -OH groups and the starch phosphoric moiety for binding of the cations. Also, in this case, drying and freezing/thawing of the granules caused higher uptake of Cu<sup>2+</sup>, compared to that of the native starch. Incorporation of Cu<sup>2+</sup> into the granules influenced the thermal behavior of starch. As was found in the DSC measurements performed for the samples soaked in copper acetate solution, the water evaporation enthalpy, equal -49.5 to -55.6 kJ mol<sup>-1</sup> (compared to -39.8 kJ mol<sup>-1</sup> for free water molecules (22)), was not affected by the cations present in the granules. This supports the conclusion that, in acetate solution, coordination of the Cu<sup>2+</sup> occurred mainly to the crystalline part of the polysaccharide matrix. TGA coupled with SDTA revealed that the copper ions changed the thermal stability of the granules (Table 2). Thus, a significant increase of the starch decomposition enthalpy (in the range of 400-1000%) accompanied by a decrease, of about 20 °C, of the starch decomposition temperature was observed (Table 2, Figure 2a). Moreover, decomposition was less effective in the presence of copper than in the native starch samples (about 70% and 77% of the sample mass, respectively) (Figure 2b). An exothermic effect, observed in the appropriate DSC course, pointed to a catalytic influence of Cu<sup>2+</sup> on starch thermal decomposition occurring under very



**Figure 2.** (a) DSC course of the studied starch and starch + copper acetate samples. (b) TG/DTG course of the studied starch and starch + copper acetate samples.



**Figure 3.** QMS course for the investigated starch samples.

low oxygen content (less than 0.001%). In such conditions,  $\text{Cu}^{2+}$  ions could act as an oxidizing agent (the standard potential ( $E^\circ$ ) of the reaction  $\text{Cu}^{2+} + e \leftrightarrow \text{Cu}^+$  is equal to +0.153 V (24)). Therefore, decomposition of the polysaccharide began at a lower temperature compared to that of the native starch samples. This explanation could be supported by the results of the simultaneous mass analysis of the gas evolved during the starch decomposition, in particular by the high and well-resolved peaks in the obtained QMS spectra representing the evolution of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  molecules during the decomposition process (Figure 3).

The obtained results show the complexity of the cation sorption occurring in starch granules. Nevertheless, the study provides new information about starch–salt solution interactions, supporting our understanding of starch properties. The influence of the counteranions, present in the solution, on the accumulation of  $\text{Cu}^{2+}$  by native starch granules should be taken

into account while using copper salts in environmental and agricultural applications.

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