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Determination of the phosphorus content in potato starch using an energy-dispersive X-ray fluorescence method

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Abstract

Potato starch is unique because of its high starch phosphorus content. The textural characteristics of potato starch change due to the presence of the starch phosphate. Thus, the measurement of phosphorus in potato starch is needed, but conventional methods require a considerable amount of time and labour. In this investigation, a simple and fast analytical procedure has been developed for the determination of the phosphorus content of potato starch with a non-destructive energy dispersive X-ray fluorescence (ED-XRF) technique. Potato starch samples were analyzed as pressed pellets using detection times of 200 s. Reference values, measured by a conventional method, namely, wet chemical analysis, were used to calibrate the ED-XRF. Calibration was done using 20 potato starch samples, and the results were validated using a second set of 15 samples. The results indicated the validity of ED-XRF as a rapid and non-destructive method for the quantitative determination of phosphorus content of potato starch. Based on the combined results of ED-XRF and Rapid Visco-Analyzer (RVA), ED-XRF is promising for predicting the peak viscosity, by RVA, of potato starch paste through the measurement of starch phosphorus content.

Keywords: Potato starch; Phosphorus content; X-ray fluorescence; Non-destructive method

1. Introduction

Native starches contain small amounts of covalently bound phosphate. The degree of starch phosphorylation alters largely with the botanical origin of the starch and has a great influence on the textural characteristics of the starch. Potato starch is more highly phosphorylated than starches from other botanical sources (Hizukuri, Tabata, & Nikuni, 1970). The presence of phosphate in potato starch results in the high viscosity and transparency of its gel. Thus, potato starch is preferred for use in fish-paste products and as an ingredient in noodles. More importantly, phosphoryl-oligosaccharides, which have received much attention regarding their functional properties, are produced in the degradation of potato starch by amylase (Kamasaka et al., 1995). Potato starch, with a higher phosphorus content, is attractive for the effective production of phosphoryl-oligosaccharides. The phosphorus content in potato starch changes significantly, according to the cultivars (Haase and Plate, 1995; Kim, Wiesenborn, Orr, & Grant, 1996; Noda et al., 2004a, 2004b; Veselovsky, 1940; Wiesenborn, Orr, Casper, & Tacke, 1994) and environmental factors (Haase and Plate, 1996; Noda et al., 2004a, 2004b). Our previous data, using a total of 96 potato starches, indicated that the phosphorus content ranged from 510 to 1334 ppm and that the phosphorus content was positively correlated with the peak viscosity and breakdown (Noda et al., 2004a).

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Therefore, it is important to monitor the level of phosphorus in potato starch with a precise, rapid, and simple method for the high utilization of potato starch. For the determination of phosphorus content in starch, wet chemical analysis is the most commonly used method. However, this method is time-consuming and not necessarily suitable for screening of phosphorus content of starch.

Energy dispersive X-ray florescence (ED-XRF) is a promising analytical technique for determining element contents. This method can be directly applied in dried and pelletized samples, avoiding sample digestion dissolution by toxic and corrosive acids. Furthermore, the short analysis time required for this method makes it suitable for routine analysis. In recent years, XRF has been used for various solid food materials, such as spices (Joseph, Lal, Bajpai, & Mathur, 1999), bread improvers (Ekinci, Ekinci, & Sahin, 2002), tea (Salvador, Lopes, Filho, & Zucchi, 2002), milk powder (Alvarez & Mazo-Gray, 1990, 1991), and milk-based products (Perring & Andrey, 2003). However, none of the reports mentioned the application of ED-XRF for the measurement of the elements in starch samples.

This study describes the application of ED-XRF for the rapid and non-destructive determination of phosphorus content and the prediction of the pasting characteristics in potato starch samples.

2. Materials and methods

2.1. Starch samples

Nine potato starch samples were used for the test regarding the effect of pelletization on X-ray intensity counts. Of the nine, three were products of the Nakashari Starch Factory, Shari Agricultural Cooperative Association, Shari, Hokkaido, Japan, and one was from the Jinno Starch Co., Sarabetsu, Hokkaido, Japan. The others were isolated from five potato samples harvested at the experimental farm at the National Agricultural Research Center for the Hokkaido Region at Memuro, Hokkaido, Japan. Starch isolation was performed by a previously reported method (Noda et al., 2004b). Thirty-five potato starch samples were used for the calibration model. Of the 35, four were the products of the Nakashari Starch Factory, Shari Agricultural Cooperative Association, Shari, Hokkaido, Japan, and five were from the Jinno Starch Co., Sarabetsu, Hokkaido, Japan. The others were isolated from 25 potato samples harvested at the experimental farm at the National Agricultural Research Center for the Hokkaido Region at Memuro, Hokkaido, Japan. Thirty five potato starch samples were divided into two sets: one set, including 20 samples, was used for calibration in order to develop the model; the other, including 15 samples, was used for validation, i.e., to test the model. A total of 69 potato starch samples, harvested at the experimental farm at the National Agricultural Research Center for the Hokkaido Region at Memuro, Hokkaido, Japan, was used for the determination of phosphorus content using the newly developed ED-XRF method.

2.2. Granule size

As for the nine potato starch samples used for the test regarding the effect of pelletization on X-ray intensity counts, the granule size distribution of starch was determined using Sympatec HELOS particle-size analysis. The median granule size, based on volume distribution was measured.

2.3. RVA analysis

For the 69 potato starch samples used for the determination of phosphorus content using the ED-XRF method, the RVA pasting viscosity was determined as described previously (Noda et al., 2004b).

2.4. Phosphorus content by standard analysis

The phosphorus content of the starch sample was determined as inorganic phosphorus after treatment with hot HNO_3-perchloric acid using the vanado-molybdate method, as described previously (Noda et al., 2004b).

2.5. Phosphorus content by ED-XRF analysis

For the pelletized sample, each starch (about 2 g) was pressed into thin pellets of 10 mm diameter. For the non-pelletized sample, each starch (about 7 g) was weighed into a disposable sample container. The quantitative analysis of phosphorus was done at an accelerating voltage of 15 kV, and at a detection time of 200 s with a Horiba MESA-500 W EDX spectrometer. The number of P Kα counts per second (cps/μA) was detected.

3. Results and discussion

Wet chemical analysis is commonly used to determine the phosphorus content in starch. Starch samples are digested with HNO_3 and perchloric acid, and the amount of phosphorus in the digested samples is measured by the Fiske–Subbarow method (Fiske & Subbarow, 1925) or the vanado-molybdate method (Noda et al., 2004b). However, chemical analysis has disadvantages. First, it is a time-consuming method that requires the disposal of toxic and corrosive acids. Second, the combined use of HNO_3 and perchloric acid requires caution to avoid the explosion of these acids on heating. We attempted to apply the ED-XRF method to determine the level of phosphorus in potato starch and to develop a non-destructive method that is more convenient and safer for collecting data than wet chemical analysis. ED-XRF spectra were recorded using potato starch samples. The spectra were analyzed to obtain the number of P Kα counts per second with the aim of determining the phosphorus content in potato starch. We also obtained the reference values of phosphorus content by the conventional method, namely, wet chemical analysis, and these values were used to calibrate the ED-XRF. It has been reported that the granule size of potato cultivars varies significantly (Haase and Plate, 1996; Noda et al., 2004a, 2004b; Wiesenborn et al., 1994). In addition, potato starch is separated into different sizes of granules in a few starch factories. Thus, a large variation in granule size presumably exists among potato starch samples. Direct ED-XRF analysis affects the X-ray intensity counts (P Kα) due to the difference in granule size. The effect of pelletization on the X-ray intensity counts (P Kα) was examined using nine potato starch samples differing in granule size. As seen in Table 1, pelletized samples displayed higher X-ray intensity counts (P Kα) (0.0802–0.1376 cps/μA) than did non-pelletized samples (0.0429–0.0730 cps/μA). Although there was a satisfactory correlation ($R^2 = 0.955$) between the phosphorus content determined by wet chemical analysis and the X-ray intensity counts for pelletized samples, such trends were not observed for non-pelletized samples. This was because potato starch samples with a higher phosphorus content and a smaller granule size (#7, #8, and #9) gave relatively lower X-ray intensity counts (0.0484–0.0552 cps/μA) for non-pelletized samples. Based on the above results, we decided to use pelletized samples for ED-XRF analysis.

Calibration was established using 20 potato starch samples, and the results were validated using a second set of 15 samples. The best-fit model for the calibration set was found to be provided by a multiple linear regression model involving the number of P Kα counts per second, as in Eq. (1).

$$P_o = 8665 I_{\mathrm{PK}\alpha} - 158, \qquad (1)$$

where P_o is the phosphorus content (ppm) and $I_{\mathrm{P\ K}\alpha}$ is the number of P Kα counts per second (cps/μA), while

Table 1
The effect of pelletization on X-ray intensity counts (P Kα)[a]

Sample no.	Phosphorus content (ppm)	Median granule size (μm)	Intensity counts (cps/μA)	
			Non-pelletized sample	Pelletized sample
#1	621	44.4	0.0429	0.0802
#2	679	40.9	0.0508	0.0881
#3	752	36.8	0.0621	0.0931
#4	790	43.2	0.0496	0.1004
#5	834	33.5	0.0598	0.1027
#6	997	38.3	0.0730	0.1260
#7	1011	21.2	0.0552	0.1261
#8	1032	19.2	0.0484	0.1169
#9	1090	13.5	0.0490	0.1376

[a] Values are means of two determinations.

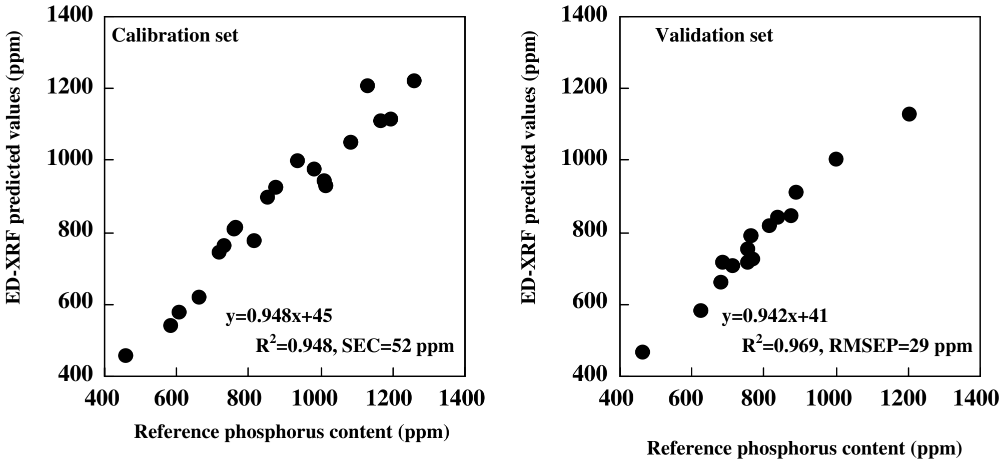

Fig. 1. Plots of ED-XRF predicted phosphorus content vs. reference phosphorus content for both the calibration and validation sets.

the coefficients of 8665 and −158 came from the least squares fitting process. Next, the standard error of calibration (SEC) and root mean standard error of prediction (RMSEP) were calculated, and SEC was 52 ppm. In addition, applying this model to a validation set gave good ED-XRF predicted values with RMSEP of 29 ppm, indicating that the model had good predictive ability. As shown in Fig. 1, a plot of the ED-XRF predicted phosphorus content for the calibration set yielded a straight line with a slope and intercept of 0.948 and 45, respectively. The R^2 value was 0.948. Similarly, the plot for the validation set is displayed as in Fig. 1, and the results of this analysis gave a straight line with a slope and intercept of 0.942 and 41, respectively, and an R^2 value of 0.969. The precision of this method was determined by a replicate measurement of one standard potato starch. As shown in Table 2, the relative standard deviation was 2.0% for 10 measurements. A relative standard deviation of 2.2 % was observed for 10 conventional measurements. The calibration curve obtained here showed a high degree of linearity over the range of 450–1250 ppm. Several researchers found the phosphorus content of various potato starches to be 630–1240 ppm (Veselovsky, 1940), 456–754 ppm (Hizukuri et al., 1970), 609–1031 ppm (Wiesenborn et al., 1994), 569–1022 ppm (Kim et al., 1995), 430–1096 ppm (Haase & Plate, 1996), and 510–1334 ppm (Noda et al., 2004a). Although very-high-amylose potato starches, generated by genetic modification, exhibited an extreme increase in the content of phosphorus (2300–3000 ppm) (Schwall et al., 2000), the case appeared to be rather extraordinary. From these results, 450 and 1250 ppm are presumably the lower and upper limits of phosphorus content in ordinary potato starch, respectively. Thus, the calibration curve is suitable for determining the phosphorus content of potato starch samples with unknown degrees of phosphorylation from ED-XRF spectra.

Table 2
Precision study of phosphorus measurement

	Phosphorus content (ppm)	
	ED-XRF method	Conventional method
	821	793
	811	840
	790	808
	803	790
	794	822
	802	812
	787	780
	778	800
	830	811
	802	790
Average	802	805
SD	16	18
RSD	2.0	2.2

Table 3
Phosphorus content and peak viscosity of potato starch samples analyzed by ED-XRF and RVA, respectively[a]

Cultivar	Phosphorus content (ppm)	Peak viscosity (RVU)
Setoyutaka	434	168
Meiho	442	200
Oojiro	457	187
Shimabara	465	230
Myojo	466	207
Benimaru	537	233
Superior	541	221
Russet Burbank	543	246
Astarte	545	265
Hokkai-aka	549	231
Shiretoko	561	230
Yukirasha	596	220
Kintoki-imo	600	237
Nishiyutaka	635	223
Hokkai No. 95	641	230
Early rose	643	268
Tarumae	648	267
Hatsufubuki	652	251
Yukijiro	652	297
Beni-akari	652	262
Youraku	656	261
Toyoshiro	657	276
Toyo-akari	659	279
Bintje	663	268
May Queen	666	283
Haruakari	673	246
Aiyutaka	682	278
Ezo-akari	684	289
Bihoro	686	268
Vermont Gold Coin	690	248
Konafubuki	708	267
Hokkai No. 90	713	280
Kitahime	721	279
Green Mountain	723	323
Dejima	726	258
Nemuromurasaki	737	261
Kachikei No. 10	741	287
Kennebec	764	307
Early Starch	770	314
Pepo	771	314
Triumph	776	279
Kita-akari	790	313
Irish Cobbler	791	276
Sakurafubuki	795	295
Hokkai No. 93	795	279
Tokachikogane	819	301
Hokkai No. 94	826	281
Musamaru	831	311
Hanashibetsu	839	308
Star Queen	840	283
Hokkai No. 89	855	288
Aino-aka	870	323
Benihisa	887	265
Snowden	888	324
Fugenmaru	889	328
Inca Purple	891	337
Hokkai No. 87	903	352
Inca Red	908	284
Hokkai No. 92	910	301

(*continued on next page*)

Table 3 (*continued*)

Cultivar	Phosphorus content (ppm)	Peak viscosity (RVU)
North Chip	933	362
Inca-no-mezame	940	314
Kachikei No. 6	963	358
White Fryer	1001	352
Atlantic	1002	389
Hokkai No. 91	1016	325
Hokkaikogane	1050	360
Kitamurasaki	1065	374
Touya	1079	385
Kachikei No. 11	1087	400
Mean ± SD	751 ± 165	286 ± 50

[a] Values are means of two determinations.

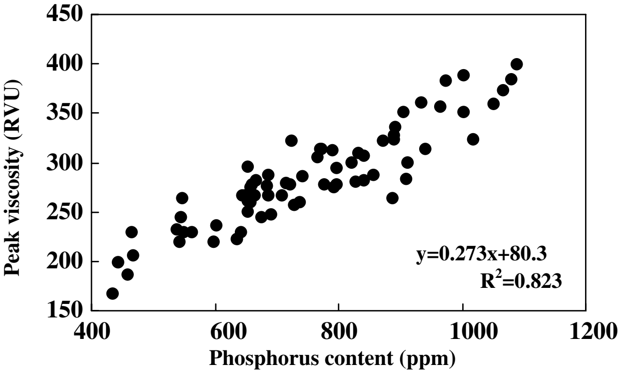

Fig. 2. Plot of phosphorus content vs. peak viscosity for 69 potato starch samples.

The ED-XRF method was used to determine the phosphorus content in many starch samples from 69 potato cultivars. The results are summarized in Table 3. The phosphorus content varied widely among the cultivars and had a mean value of 751 ppm. The lowest content was observed in Setoyutaka with 434 ppm, while the highest was in Kachikei No. 11 with 1087 ppm. The striking point is that purple- (Inca Purple, Kitamurasaki and Hokkai No. 92) and red-flesh (Inca Red and Hokkai No. 91) potato cultivars, which contain anthocyanins, had a relatively higher content (891–1065 ppm). In potato, the phosphorus content in starch has been identified as the key factor in determining the starch pasting characteristics. It has been reported that starch-bound phosphate distinctly enhances the starch-paste viscosity (Kim et al., 1995; Noda et al., 2004a, 2004b; Veselovsky, 1940; Wiesenborn et al., 1994). Therefore, there is a potential improvement when analyzing potato starch pasting properties using ED-XRF in place of RVA. To evaluate the application of ED-XRF for the rapid determination of the pasting properties of potato starch, the RVA pasting properties were also analyzed using the 69 potato starches mentioned above. As shown in Table 3, the peak viscosity ranged from 168 RVU in Setoyutaka to 400 RVU in Kachikei No. 11, with a mean value of 286 RVU. The relationship between the phosphorus content and peak viscosity analyzed by ED-XFR and RVA, respectively, is presented in Fig. 2. The regression analysis revealed a positive correlation as in Eq. (2):

$$\mathrm{PV} = 0.273\mathrm{P_o} + 80.3, \qquad (2)$$

where PV is the peak viscosity (RVU) and $\mathrm{P_o}$ is the phosphorus content (ppm), while the coefficients of 0.273 and 80.3 came from the least squares fitting process. The R^2 value was 0.823. In this investigation, the peak viscosity was closely dependent on the amounts of phosphate analyzed by ED-XRF. The analysis time of ED-XRF was shorter (200 s) than that of RVA (13 min). Thus, ED-XRF seems to be a suitable method for the rapid prediction of starch peak viscosity. As far as is known, there are few reports concerning the application of a non-destructive method to the rheological characteristics of starch.

4. Conclusions

A rapid and non-destructive ED-XRF method was developed and validated for the measurement of phosphorus content in potato starch. The ED-XRF method has been found to be a reliable technique for analyzing the phosphorus content in potato starch and has been used successfully in a range of 450–1250 ppm. The analytical results by the newly developed ED-XRF method indicated that the phosphorus content ranged from 434 to 1087 ppm for starches from 69 potato cultivars. As at higher level of phosphorus has been closely associated with higher peak viscosity of starch paste, ED-XRF also has the potential to predict the peak viscosity. The results obtained here are important for better utilization of potato starch.

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References

Alvarez, M., & Mazo-Gray, V. (1990). Determination of potassium and calcium in milk powder by energy-dispersive X-ray fluorescence spectrometry. *X-ray Spectrometry, 19*, 285–287.

Alvarez, M., & Mazo-Gray, V. (1991). Determination of trace elements in organic specimens by energy-dispersive X-ray fluorescence using a fundamental parameters method. *X-ray Spectrometry, 20*, 67–71.

Ekinci, N., Ekinci, R., & Sahin, Y. (2002). Determination of iodine and calcium concentrations in the bread improver using ED-XRF. *Journal of Quantitative Spectroscopy & Radiative Transfer, 74*, 783–787.

Fiske, C. H., & Subbarow, Y. (1925). The colorimetric determination of phosphorus. *The Journal of Biological Chemistry, 66*, 375–400.

Haase, N. U., & Plate, J. (1996). Properties of potato starch in relation to varieties and environmental factors. *Starch/Stärke, 48*, 167–171.

Hizukuri, S., Tabata, S., & Nikuni, Z. (1970). Studies on starch phosphate: Part 1. Estimation of glucose 6-phosphate residues in starch and the presence of tuber bound phosphate(s). *Starch/Stärke, 22*, 338–343.

Joseph, D., Lal, M., Bajpai, H. N., & Mathur, P. K. (1999). Level of trace elements of few Indian spices by energy-dispersive X-ray fluorescence (EDXRF) method. *Journal of Food Science and Technology-Mysore, 36*, 264–265.

Kamasaka, H., Uchida, M., Kusaka, K., Yoshikawa, K., Yamamoto, K., Okada, S., et al. (1995). Inhibitory effect of phosphorylated oligosaccharides prepared from potato starch on the formation calcium phosphate. *Bioscience, Biotechnology and Biochemistry, 59*, 1412–1416.

Kim, Y. S., Wiesenborn, D. P., Orr, P. H., & Grant, L. A. (1995). Screening potato starch for novel properties using differential calorimetry. *Journal of Food Science, 60*, 1060–1065.

Noda, T., Tsuda, S., Mori, M., Takigawa, S., Matsuura-Endo, C., Hashimoto, N., & Yamauchi, H. (2004a). Properties of starches from several potato varieties grown in Hokkaido. *Journal of Applied Glycoscience (Oyo Toshitsu Kagaku), 51*, 241–246.

Noda, T., Tsuda, S., Mori, M., Takigawa, S., Matsuura-Endo, C., Saito, K., Mangalika, W. H. A., et al. (2004b). The effect of harvest dates on the starch properties in various potato cultivars. *Food Chemistry, 86*, 119–125.

Perring, L., & Andrey, D. (2003). ED-XRF as a tool for rapid minerals control in milk-based products. *Journal of Agricultural and Food Chemistry, 51*, 4207–4212.

Salvador, M. J., Lopes, G. N., Filho, V. F., & Zucchi, O. (2002). Nascimento Quality control of commercial tea by X-ray fluorescence. *X-ray Spectrometry, 31*, 141–144.

Schwall, G. P., Safford, R., Westcott, R. J., Jeffcoat, R., Tayal, A., Shi, Y.-C., et al. (2000). Production of very-high-amylose potato starch by inhibition of SBE A and B. *Nature Biotechnology, 18*, 551–554.

Veselovsky, I. A. (1940). Biochemical and anatomical properties of starch of different varieties of potatoes and their importance for industrial purposes. *The American Potato Journal, 17*, 330–339.

Wiesenborn, D. P., Orr, P. H., Casper, H. H., & Tacke, B. K. (1994). Potato starch paste behavior as related to some physical/chemical properties. *Journal of Food Science, 58*, 644–648.