

## 미강유 중의 미량금속의 방사화분석

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### Neutron Activation Analysis of Trace Metals in Rice Bran Oil

— Determination of Manganese and Copper —

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#### 요 약

미강유의 안정성에 영향을 미칠 미량원소들 중에서 망간 및 구리를 방사화분석하였다. 망간은 TRIGA MARK II 원자로의 pneumatic tube (neutron flux =  $3.4 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ )에서 10분간 조사한 후 비파괴분석법으로, 구리는 60분간 조사한 후 음이온교환수지를 사용하는 분리법에 따라 분리하여 정량하였다.

공정별로 채취한 탈랍원유, 탄산유, 탈색유 및 탈취유를 시료로하여 분석한 결과 망간함량은 각각 13.4, 2.6, 0.24 및 0.33 ppm 이었고, 구리함량은 0.24, 0.21, 0.056 및 0.040 ppm 이었다.

정제유(탈색유 및 탈취유)의 망간함량은 대단히 많아, Privett 가 지적한, 축매로서 한계량인 0.025 ppm 에 4~13 배에 달했고, 구리는 대체로 외국의 수준이었다.

#### Abstract

With the object of checking the stability of domestic rice bran oil, manganese and copper in trace amounts were analysed by neutron activation analysis. Manganese was determined by the nondestructive method after it was irradiated at the pneumatic tube (neutron flux =  $3.4 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ ) of the TRIGA MARK II reactor for 10 min. and copper by the destructive method which uses an anion exchange resin to concentrate copper after irradiation for 1 hr.

The manganese and copper contents (along with the respective experimental standard deviations) of dewaxed crude oil, deacidified oil, bleached oil and deodorized oil, sampled from each process of one batch processing, were  $13.4 \pm 0.4$ ,  $2.6 \pm 0.2$ ,  $0.24 \pm 0.01$  and  $0.33 \pm 0.03$  and  $0.24 \pm 0.03$ ,  $0.21 \pm 0.03$ ,  $0.056 \pm 0.007$  and  $0.040 \pm 0.002$ , respectively.

The contents of manganese in domestic rice bran oil compared with that of a foreign product are extraordinarily high, while the copper contents seem to be in the similar level as the contents of foreign products.

#### 1. Introduction

It is well known that trace metals present in fat

and oil show a strong catalytic effect in the "autoxidation" of fat and oil which leads to deterioration or rancidity of fat and oil. In order to prevent fat and oil from deteriorating due to the autoxidation, man often uses a means to remove the trace metals from

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fat and oil by means of ion exchange techniques<sup>1)</sup> or to mask the trace metals by adding chelating agents<sup>2)</sup> such as citric acid (in this case such a material is called metal scavenger, metal inactivator or metal inhibitor).

In the mode of chemical action of such metals, various cases have been disclosed or inferred by many investigators. Arranged intensively, they can be divided into two kinds. In one<sup>4), 5)</sup>, the trace metals catalyse to form the hydroperoxide with the aid of other free radicals and, in the other<sup>3), 6), 7)</sup>, the trace metals catalyse the hydroperoxide to decompose and produce free radicals, which induce some chain reactions related to the autoxidation.

However, the catalytic action of metal described in the above reactions is dependent upon the content of the metal present in oil and fat, being that its action starts only when the metallic content becomes in excess of a certain amount.

For the limit of the content that shows catalytic action, there is King's report<sup>8)</sup> using lard as an object of study. It indicates that the content of each metal that effects the stability of lard at 97.8°C is as follows: Cu 0.05, Mn 0.6, Fe 0.6, Cr 1.2, Ni 2.2, Zn 19.6, Al 50 ppm. Privett<sup>9)</sup> reported that, in the autoxidation of methyl linoleate, when the content of iron or copper chloride is less than 1 ppm, these metals show no effect, but the low valency salts of cobalt and manganese do so with only 0.025 ppm.

In order to check the stability of domestic rice bran oil, it was attempted to confirm the kinds of trace metals contained in domestic rice bran oil and to determine their contents.

After examining some of the literatures, as the trace metals which have a great possibility of being present in fat and oil and which take part in the autoxidation of fat and oil, the following metals were selected: Fe<sup>16), 1), 13)</sup>, Mn<sup>1)</sup>, Cu<sup>1), 11), 14)</sup>, Co<sup>13)</sup>, Ni<sup>13)</sup>, Al<sup>18)</sup>. Among these metals, at first, Mn and Cu were picked for study.

In the range below 1 ppm, the available analytical methods usually involve dry or acid-wet ashing<sup>10)</sup> to concentrate the trace metals for subsequent analysis. The dry ashing spectrographic procedure is cumbersome and time-consuming. Furthermore, there is a

serious problem due to the loss of volatile metal complexes<sup>15)</sup> with most ashing procedures and the contamination of chemicals to be used. Therefore, it is important to use a rapid and sensitive analytical method, not involving ashing procedures, to be applied to fat and oil. As a method suitable to achieve the above aim, the neutron activation analysis was selected from various methods.

The activation reactions used in the analysis are  $^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$  and  $^{63}\text{Cu}(n, \gamma)^{64}\text{Cu}$ . The nuclear properties of the activated manganese and copper and the comparison of the limit of detection of activation analysis with that of spectrophotometric analysis are shown in Table I.

**Table I. Nuclear characteristics of metals activationally analysed and comparison of limit of detection of activation analysis with that of spectrophotometric analysis.**

Characteristics	Manganese	Copper
Natural isotope	$^{55}\text{Mn}$	$^{63}\text{Cu}$
Natural abundance (%)	100	69.1
Cross section (barn)	13.3	4.5
Isotope produced	$^{56}\text{Mn}$	$^{64}\text{Cu}$
Half life of isotope produced (hr.)	2.58	12.9
$\gamma$ energies of isotope produced (MeV)	0.845*	0.511*
	1.81	1.34
	2.11	
Comparison of limit of detection ( $\mu\text{g}$ ) <sup>17)</sup>		
Activation analysis**	$1 \times 10^{-4}$	$5 \times 10^{-3}$
Spectrophotometric (method)	5 (permanganate)	2 (dithizone)
* Photopeak used in the measurement of activity		
** Practical conditions: $\phi = 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ , irradiation time = 6-600 min., cooling time = 30-60 min.		

Several activation methods for the determination of copper in fat and oil have been reported in some literatures. They are Hirai<sup>11)</sup>, Høgdahl<sup>12)</sup> and Shinbori et al.<sup>14)</sup>. Hirai's method is applied to copper in myristic acid and hardened oil, Høgdahl's method to hydrogenated fats and Shinbori's method to refined soybean oil. The sample, Shinbori et al. analysed, is similar to the sample used in this experiment, but they used  $\beta$ -ray of energy 0.57 MeV as detecting radiation.

In this report, manganese is analysed by nondestructive neutron activation analysis and copper is an-

analysed by Hirai method modified by authors to be applied to rice bran oil.

## 2. Experimental

### 2.1. Samples

The samples were presented by Hwa Sung Industrial Co. and Heuop Seong Oil Co. in Seoul. Their sorts and characteristics were given in Table II.

Table II. Characteristics of samples of rice bran oil.

Sample	Mark of sample	Saponification value	Acid value	Iodine value
Dewaxed crude oil	C-O	182	62.0	99
Deacidified oil	Da-O	186	5.3	103
Bleached oil	B-O	186	6.0	110
Deodorized oil	Do-O	186	5.0	112
Dewaxed crude oil	C-O-D	184	53.2	103
Deodorized oil	Do-O-D	187	4.6	119

One company offered C-O, Da-O, B-O and Do-O. These are samples taken from each process of one batch processing. Another company offered C-O-D and Do-O-D. C-O-D and Do-O-D correspond to the C-O and Do-O of the former company, respectively.

### 2.2. Standards

The Standards, which were irradiated with a sample, were prepared as follows:

Manganese. John Matthey Co. made manganese metal 0.0110 gr was accurately weighed, dissolved in 10 ml of dil.  $\text{HNO}_3$  solution (1:1) and diluted to 100ml (110  $\mu\text{g}/\text{ml}$ ). Another standard was made by diluting 1 ml of the above standard solution to 10ml (11.0  $\mu\text{g}/\text{ml}$ ).

Copper. Electrolysed copper 0.0164 gr was accurately weighed, treated in the same manner mentioned above and diluted to 1000ml (16.4  $\mu\text{g}/\text{ml}$ ). Another standard was made by diluting 1  $\mu\text{g}$  of the above standard solution to 10 ml (1.64  $\mu\text{g}/\text{ml}$ ).

### 2.3. Measurement of Energy and Activity

Measurements of energy and activity of  $\gamma$ -ray were accomplished with Gammascopes II, model 102, 100-channel pulse height analyser (Technical Measurement

Corporation) coupled with a 2'' $\times$ 2'' NaI(Tl) crystal. Measurements were made at 17.0 KeV per channel and with the source separated from the detector by a 0.5'' polyethylene  $\beta$  absorber.

### 2.4. Nondestructive Analysis of Manganese

One gr of a sample was accurately weighed in a polyethylene vial, tightly sealed and placed together with a standard in a plastic container, rabbit (2.0 $\times$ 11.5 cm). The rabbit is transferred to the pneumatic tube of TRIGA MARK II reactor, which permits irradiation at thermal neutron fluxes of  $3.4 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ , through the pneumatic transfer system within 8 sec and irradiated for 10 min. After cooling for 1 hr., the sample was transferred to a test tube for  $\gamma$  spectrometry. The  $\gamma$  spectra were obtained at different times to check the decay.

### 2.5. Destructive Analysis of Copper

#### 2.5.1. Irradiation

One to 1.5 gr of sample was placed in a polyethylene vial washed thoroughly with 6N HCl solution and tightly sealed. The sample and a standard were packed side by side into a rabbit and irradiated for 1 hr. in the pneumatic tube.

#### 2.5.2. Radiochemical Separation

After irradiation, the sample was cooled for 30 min. and the cover of the vial was removed. The uncovered vial in which the sample was contained was accurately weighed. The weighed sample was poured into 20 ml of *n*-hexane in 100 ml-separatory funnel. The empty vial was accurately weighed again. Nine ml of 6N HCl and 1 ml of copper carrier solution (cupric nitrate, 19.72 mg/ml as Cu) were added to the separatory funnel and violently shaken for 1-2 min. When the organic solvent and 6N HCl solution were separated from each other, the acid phase was transferred into a 50 ml-beaker. The organic phase was treated once more in the same manner and the acid phase was combined with the former acid solution. To remove suspended oil, the acid phase was filtered on a wet filter paper. Two or three drops of 30%  $\text{H}_2\text{O}_2$  are added to the filtrate and the filtrate was carefully concentrated to about

10 ml on a heating plate. The above solution was passed through an anion exchange resin (Amberlite 400 (Rohm & Haas Co.)) column (shown in Fig.1) which had been treated with 20ml of 8N HCl beforehand.

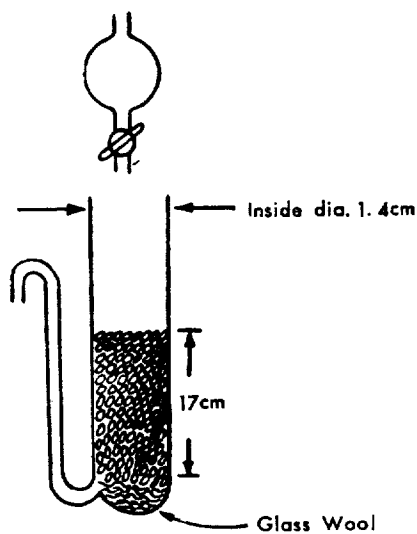


Fig. 1. Anion exchange resin column for Concentration of copper ion.

The resin was washed with 30 ml of 8N HCl and next with 30 ml of 6 N HCl and then with 20ml of 4 N HCl. The effluents were discarded (the color of these effluents was yellow, but when the feeding of 4N HCl was almost finished, the effluent of blue-yellow color appeared). Next, 50ml of 2 N HCl was passed through and the eluate was collected. The eluate was diluted to about 70 ml with water and then heated to 60-70°C. Here  $H_2S$  gas was led for 5-6 min. to precipitate copper. The obtained precipitate was filtered with filtration apparatus (with the demountable bottom) under reduced pressure by an aspirator, washed with water and acetone, dried and mounted.

Separately, the amount of standard which was determined by preliminary experiments was taken out of the irradiated standard solution, made to infiltrate into a piece of filter paper which was cut to the same size as the filter paper used in the precipitation of sample, dried and mounted.

### 2.5.3. Determination of chemical yield

The chemical yield (recovery) of the precipitate obtained in 2.5.2. was determined as follows: 100  $\mu$ l of  $Cu(NO_3)_2$  solution (199.7  $\mu$ g/ml as Cu) as a standard was made to infiltrate into the filter paper which was cut out in the same size as the filter paper on which the precipitate of the sample is filtered. The precipitate obtained in 2.5.2. was cooled for some periods until its activity was reduced to the negligible amount (about 5 days). The standard and the precipitate were prepared to have the same geometry. They were placed side by side in the rabbit and irradiated at the pneumatic tube for 3 sec. The chemical yield was calculated from the activity.

## 3. Results

The data are presented in Table III along with the respective experimental standard deviations which, in most cases, were found to be better than  $\pm 10\%$ .

Table III. Results of determination of Mn and Cu in rice bran oils (ppm).

Sample	Manganese	Copper
C-O	$13.4 \pm 0.4$	$0.24 \pm 0.03$
Da-O	$2.6 \pm 0.2$	$0.21 \pm 0.03$
B-O	$0.24 \pm 0.01$	$0.056 \pm 0.007$
Do-O	$0.33 \pm 0.03$	$0.040 \pm 0.002$
C-O-D	$13.2 \pm 0.7$	$0.16 \pm 0.01$
Do-O-D	$0.11 \pm 0.01$	$0.026 \pm 0.002$

The experimental standard deviations were determined from three or four independent measurements.

Some cases reported in foreign countries are shown in Table IV.

Table IV. The content of Mn and Cu reported in the foreign countries (ppm).

Samples	Manganese	Copper	Reference
Crude soybean oil	0.25	0.085	1
Demetalized soybean oil	0.000	0.017	1
Myristic acid(1st grade reagent)		0.026	11

Hardened oil(technical grade)	0.086	11
Hydrogenated fat	0.026-0.07	12
Refined soybean oil	0.02-0.09	14
Crude soybean oil	0.12-0.14	10
Crude rape seed oil	0.09	10

When the manganese contents of domestic dewaxed crude rice bran oils were compared with that of a foreign product, though the sample is not of the same kind, those of domestic products were found to be extraordinarily high. The manganese contents of domestic refined rice bran oil are 4-13 times more than 0.025 ppm which, Privett<sup>9)</sup> pointed out, is the limit of content that shows catalytic action. Therefore, in order to improve the stability of domestic rice bran oil, it is thought that much attention should be given to the manganese content. In the case of copper, it seems to be on the similar level as the contents of foreign products.

#### 4. Discussion

It seems that manganese is able to be determined more easily than any other methods within shorter time.

In the determination by this method,  $^{56}\text{Fe}(n, p)$   $^{56}\text{Mn}$  and  $^{59}\text{Co}(n, \alpha)^{56}\text{Mn}$  of iron and cobalt present in the sample may occur and the errors by these reactions should be necessarily considered. But, because the cross sections of both interfering nuclear reactions are very small, 0.44mb<sup>20)</sup> and 0.14 mb<sup>20)</sup>, respec-

tively, and the difference between the flux<sup>21)</sup> of the thermal and fast neutrons is slight,  $3.4 \times 10^{12}$  and  $4.8 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ , respectively, in fact, their effects are negligible. If it is supposed that iron and cobalt are contained in the same amount as manganese in the sample, each calculated contribution is  $4.2 \times 10^{-3}\%$  and  $1.4 \times 10^{-3}\%$ , respectively. As a practical example, in the case of the contents of metals of crude soybean oils reported by Viogue et al.<sup>1)</sup>, the contents of iron are 3.13-12.5 times more than those of manganese. In the case of refined soybean oils reported by Shinbori<sup>13)</sup>, the contents of cobalt are 0.01-0.04 ppm.

The effect of magnesium as another source of errors can not be overlooked, because  $^{27}\text{Mg}$  formed by the reaction  $^{26}\text{Mg}(n, \gamma)^{27}\text{Mg}$  emits the  $\gamma$ -ray of the same energy of 0.845 MeV as  $^{56}\text{Mn}$ . Especially, in the determination of the oil of a high concentration of chlorophyll which contains magnesium as its constituent, attention should be paid to. To investigate the degree of its contribution to the peak of 0.845 MeV of  $^{56}\text{Mn}$ , the decay of irradiated sample, C-O-D, was checked at different time intervals. Fig. 2 shows its results. The cpm of time 0 is the value that was counted at 7 min. after irradiation. It can be seen that even in the beginning time of decay its contribution is negligible.

The determination of copper had to be carried out by the destructive method because the peak of the  $\gamma$ -ray spectrum of copper was interfered by those of other materials.

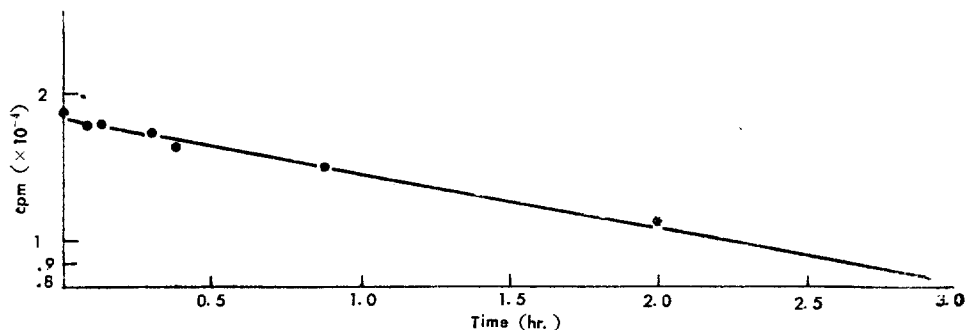


Fig. 2. Decay curve of the peak of 0.845 MeV of irradiated sample, C-O-D.

The method for separation of activated copper, namely recoil atom, is based on the Szilard-Chalmers process. In the report <sup>19)</sup> by Brune, the data about the extractable amount of activated copper from irradiated biological sample, for example, liver tissue, by HCl solution together with carrier is described to be 93%. But, in the report by Hirai<sup>11)</sup>, the recovery of copper by the Szilard-Chalmers process, wet-ashing method with conc. mixed mineral acid and dry-ashing method with  $Mg(NO_3)_2$  are compared with one another and it is described that appreciable difference among the experimental data from the three methods could not be found.

The importance of the interfering nuclear reaction,  $^{63}Zn(n, p)^{63}Cu$ , becomes great in the analysis of copper, because the cross section of zinc for fast neutron, 35mb<sup>20)</sup>, is relatively large and its content is much. Under the same supposition as in the determination of manganese, its calculated contribution amounts to  $7.6 \times 10^{-1}\%$ . As a practical example, in the reference<sup>1)</sup> it is seen that the ratios of zinc to copper are 1.45-1.65. But, in this report the error due to this interfering reaction is not considered, because the error has only a small extent of effect on the second effective figure of two effective figures of this report's experimental data. It is thought that the data should be calibrated as much as  $^{64}Cu$  formed by the interfering reaction, more correct and precise data being required. It can be accomplished by shielding the sample with cadmium metal from the thermal neutrons and making only the reaction by fast neutrons possible.

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