Effect of Water Treatment Sludge (WTS) on Trace Metals Content in Sorghum (*Sorghum bicolor* (L.) Moench).

II. Measuring of Nickel Content of the Forage

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수수 (*Sorghum bicolor* (L.) Moench)의 미량 광물질 함량에 관한 정수 슬러지 처리 효과

II. 니켈 함량 분석

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요　약

수수(*Sorghum bicolor* (L.) Moench) 잡종의 미량(微量) 광물질(鑛物質) 함량에 미치는 정수장(淨水場) 슬러지의 영향에 관해 조사를 했는데, 이번 보고는 니켈 성분의 분석에 관한 것이다. 대조구(對照區), 부숙(腐熟)시킨 정수장 슬러지, 정수장 슬러지+질소－인산－칼륨 비료, 부숙시킨 슬러지+질소, 인산, 칼륨 비료의 4가지를 처리로 하였고, 1, 3, 5시간 예열(豫熱) 시간이 실험 조건이었다. 5시간 이후의 조건에서 백그라운드의 값이 가장 적었고, (측정값들의 흡광도의 평균/측정값들의 흡광도 표준편차)의 값이 가장 커서, 5시간 예열이 좋다고 보여지며 그 이유는 니켈(Ni)의 결합력이 구리(Cu), 마그네슘(Mg), 칼슘(Ca), 칼륨(K)보다 크기 때문이라고 보여진다.

(**Key words** : Alum, Nickel, Sorghum, Spectrophotometer, Warming)

I. INTRODUCTION

While nickel (Ni) was not much researched for nutrient for plant (Kanwar and Youngdahl, 1985). There is considerable recent speculation that Ni may be essential possibly in plant metabolism (Mengel and Kirkby, 1978), and it was a nutrient for animal (McDonald et al., 1985).

Huheey et al. (1993) described that Ni, a kind

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of transition metal, has some properties as follows; 1) biological functions as an essential trace element. Chicks and rats raised on deficient diet show impaired liver function and morphology; stabilizes coiled ribosomes. Active metal in several hydrogenases and plant ureases. 2) toxicity; very toxic to most plants, moderately so to mammals; carcinogenic. 3) local industrial pollutant of air and water.

Pinta et al. (1979) described for analysing minor minerals such as copper (Cu) and nickel (Ni) with the method of atomic absorption spectrometry. Water Treatment Sludge (WTS) was utilized for the growth of Altari radish (*Raphanus sativus*) (Chang et al., 1993), and for sorghum hybrid(Kim et al, 1997; Kim et al, 2000). For trace metal of the sorghum hybrid (*Sorghum bicolor* (L.) Moench), Pioneer 931, Cu content was investigated (Choi et al., 2007).

We, the researchers, are accustomed to analyse the trace metal directly after the start of the atomic absorption spectrophotometer. In this study, the effects of warming time of atomic absorption spectrophotometer were investigated to improve the accuracy of Ni measurement in the forage.

Ⅱ. MATERIALS AND METHODS

The other materials and methods were already described in our previous reports (Chang et al., 1993 b; Kim et al., 1997; Kim and Chang, 2000; Choi et al., 2007).

In the class of *Katchug Sayanghag* (Animal feeding and its experiment), the analyses of nickel (Ni) was carried out in a laboratory at Department of Companion Animal and Animal Resources Science in Joongbu University from October 2 through October 19, 2007.

Samples were air-dried and milled for analysis of Ni. Then, a half gram each of milled sample was extracted for 18 hours by 25 ml of 1M hydrochloric acid, and adequate volume of extracts was diluted with distilled water, and filtered (Kim, 1988). While this extracting method was originally for K or Mg determination, it was used for Ni element on the present experiment. The Ni analysis was made with an atomic absorption/flame emission spectrophotometer (AA-680, Shimadzu Co. Ltd., Kyoto), with the method of atomic absorption spectrometry(Pinta et al, 1979) The condition was as follows:

Wave length, 232.0 nm; mode, Back Ground Correction (BGC); lamp current, 4 mA; slit, 0.15 nm; lamp height, 6 mm; acetylene flow, 1.7 l/min.

In order to draw calibration curve of standard solutions for Ni, the solutions were calculated three times with the AA-680 as follows;

1) 1 hour warming up of the atomic absorption spectrophotometer,

2) 3 hours warming up,

3) 5 hours warming up.

Two values are obtained on metal analysis with the AA-680 spectrophotometer; absorbance and background values for standard solutions and for samples. Therefore, in Fig. 1, 2, and 3, there are three lines; absorbance of each standard solution (Y1), range of background values using mean and standard deviation (SD) of the background (Y2) on the condition of back ground correction (BGC) mode, and range of observed absorbance values of twenty-two samples (Y3).

For comparing those results with three different warming times through the AA-680, mean and standard deviation (SD) of background values were calculated. Each coefficient of

regression and each value of correlation of the standard solutions were calculated (Son and Park, 1999).

Ⅲ. RESULTS

Table 1 shows the concentration and their absorbances of nickel (Ni) standard solutions,

Table 1. The concentration and their absorbances of nickel standard solutions, measured on 1 hour warming up of the AA-680 spectrophotometer

Number of standard solution	Ni concentration (ppm)	Absorbance
1	0.00	0000
2	0.05	0040
3	0.10	0070
4	1.00	0660

measured on 1 hour warming up of the apparatus.

Fig. 1 shows images of Ni analysis 1 hour warming up of the AA-680, which include the calibration curve of the standard solutions showing their each absorbance and Ni concentration. From the Fig. 1, we obtained results as follows;

(1) On the condition of 1 hour warming up after the start of the apparatus, absorbance of the samples has lower range; (0~30),

(2) one hour after the start, range of background values was the lowest among the three conditions, including minus values; -5.4 ± 21.5 ($-26.9 \sim +16.1$), and half of the range of the absorbance values of 22 samples were doubled with or shaded by the background values. The fact shows that the Ni analyses might be incorrect.
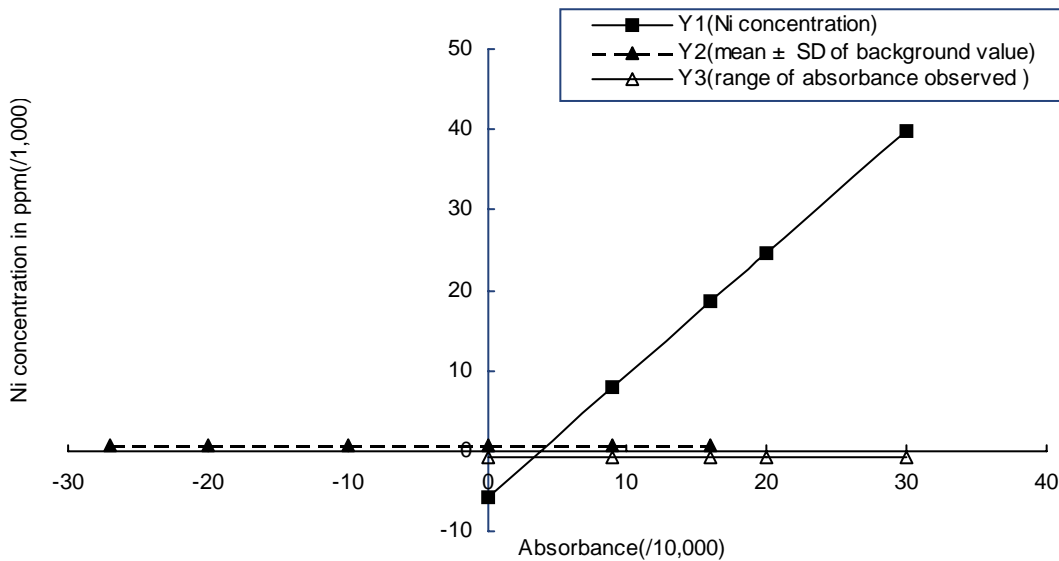

Fig. 1. Images of nickel(Ni) analysis on 1 hour warming up of the AA-680.

$Y1 = (1.5231\ X - 5.7124) \times 10^{-3}$, (r= 0.9999 **),
Y1 is Ni concentration in ppm(/1,000), r is correlation coefficient, and ** shows the significance level at 1% level, respectively. Y2 is from (mean+SD) to (mean-SD) of background values, Y3 shows the range of absorbance of the calculated samples(/10,000). Here, X is value of absorbance.

Table 2. The concentration and their absorbances of nickel standard solutions, measured on 3 hours warming up of the AA-680 spectrophotometer

Number of standard solution	Ni concentration (ppm)	Absorbance
1	0.0	− 0010
2	0.1	0060

Table 2 shows the concentration and their absorbances of nickel (Ni) standard solutions, measured on 3 hours warming up of the atomic absorption spectrophotometer.

Fig. 2 shows images of Ni analysis 3 hours warming up of the apparatus, AA-680, and the Fig. include the calibration curve of the standard solutions showing their each absorbance and Ni concentration. From the Fig. 2, we obtained the as follows;

(3) On the condition of 3 hours warming up of the spectrophotometer, range of the value of absorbances was the widest among the three warming times; (10-100),

(4) three hours warming up of AA-680, the range of background value was 25 ± 23, the range was the widest among the three conditions, and a half of the background values located in the absorbances observed.

Table 3 shows the concentration and their absorbances of nickel (Ni) standard solutions, measured on 5 hours warming up after the start of the apparatus, AA-680 spectrophotometer.

Fig. 3 shows images of Ni analysis 5 hours warming up of AA-680, and the Figure contained the calibration curve of the standard solutions with their each absorbance and Ni concentration. From the Fig. 3, we obtained the results as follows;
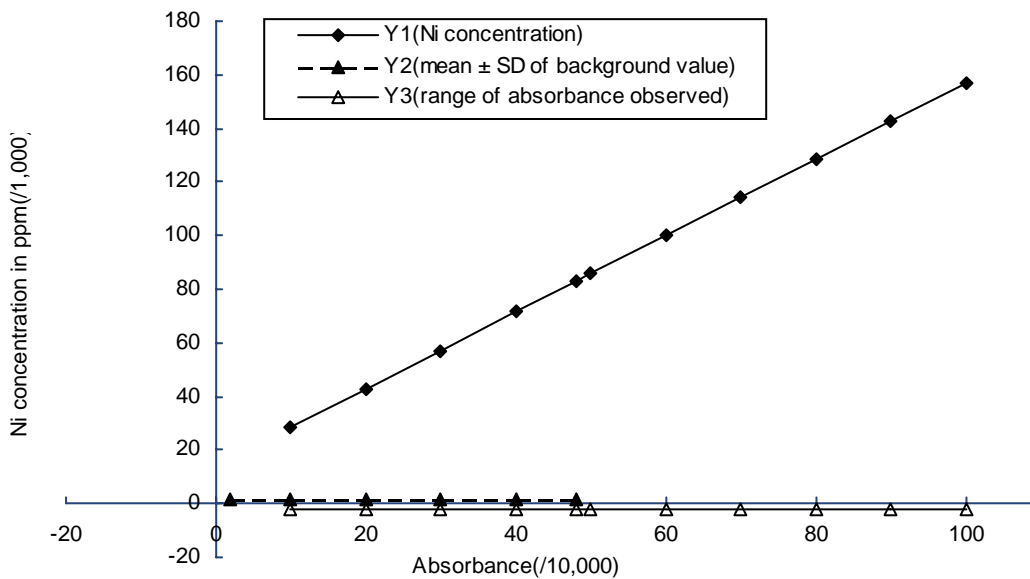
(5) On the condition of 5 hours warming up

Fig. 2. Image of nickel(Ni) analysis on 3 hours warming up of the AA-680.

$Y1=(1.4285\ X + 14.2857) \times 10^{-3}$, (r = 1.0 NS),
Y1 is Ni concentration in ppm(/1,000), r is correlation coefficient, and NS shows Not Significant(NS) at 5% level, respectively. Y2 is from (mean+SD) to (mean-SD) of background values, Y3 shows the range of absorbance of the calculated samples(/10,000). Here, X is value of absorbance.

Table 3. The concentration and their absorbances of nickel standard solutions, measured on 5 hours warming up of the AA-680 spectrophotometer

Number of standard solution	Ni concentration (ppm)	Absorbance
1	0.0	0000
2	0.1	0060
3	0.5	0350

of the spectrophotometer; narrower range (12~48) than that on the 3 hours,

(6) five hours warming up, the range of back ground value was the highest and the narrowest; 811 ± 11. There was no background value doubled with the absorbances observed, because the background values surpassed the range of

absorbances observed.

Table 4 shows the absorbance with an AA-680 spectrophotometer using the samples of sorghum hybrid (*Sorghum bicolor* (L.) Moench); absorbance on 1, 3, 5 hours warming up of the apparatus, AA-680, respectively.

Ⅳ. DISCUSSION

There is an interesting group of trace elements, called *ultratrace elements* because they are needed only little amount. These ultratrace elements include arsenic (As) and nickel (Ni), certainly essential at these low concentrations, and cadmium (Cd) and lead (Pb), probably not essential. Naturally, determination of the essentiality of an ultratrace element is even more difficult
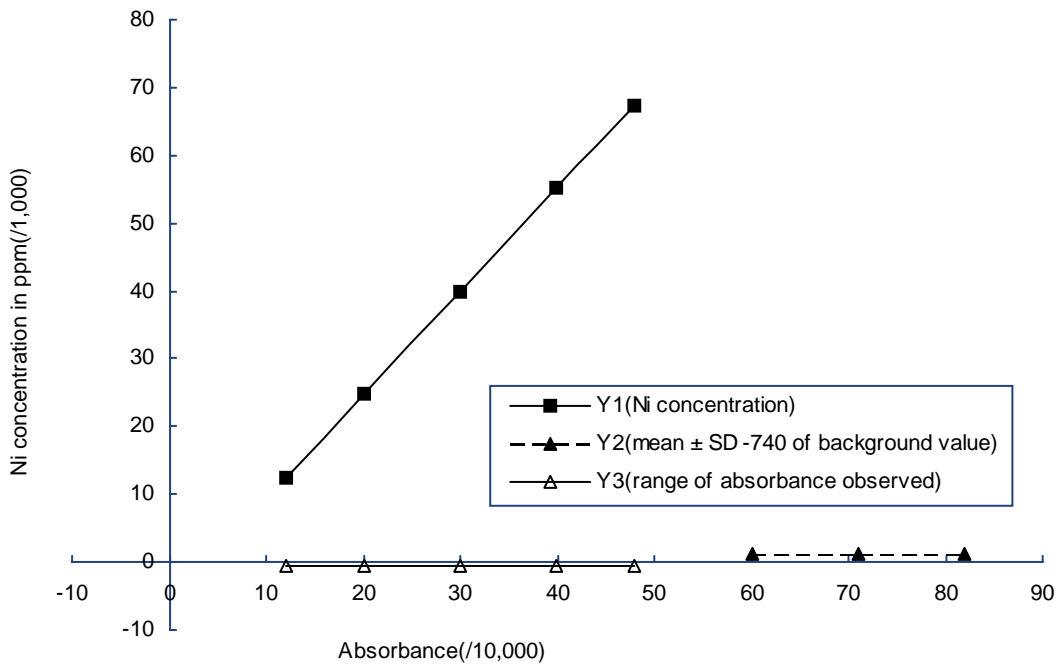

Fig. 3. Images on nickel(Ni) analysis on 5 hours warming up of the AA-680.

$Y1= (1.4129\ X - 6.8981) \times 10^{-3}$, $(r = 0.9995^*)$
Y1 is Ni concentration in ppm, r is correlation coefficient, and * shows the significance level at 5% level, respectively. Y2 is from (mean+SD) to (mean−SD) of background values, Y3 shows the range of absorbance of the calculated samples. Here, X is value of absorbance

Table 4. The absorbance with an AA-680 spectrophotometer using the samples of sorghum hybrid (*Sorghum bicolor* (L.) Moench)

Treatment No.	Absorbance 1 *	Absorbance 2 *	Absorbance 3 *
Control 1-1	000	090	047
Control 1-2	000	100	043
Control 2-1	010	060	040
Control 2-2	020	060	046
Compost 1-1	000	100	034
Compost 1-2	000	090	048
Compost 2-1	010	040	030
Compost 2-2	030	050	036
Compost 3-1	010	080	039
Compost 3-2	010	080	012
Alum + NPK 1-1	020	090	039
Alum + NPK 1-2	020	090	023
Alum + NPK 2-1	000	070	013
Alum + NPK 2-2	000	070	038
Alum + NPK 3-1	000	030	028
Alum + NPK 3-2	010	040	039
Compost + NPK 1-1	010	020	038
Compost + NPK 1-2	000	010	029
Compost + NPK 2-1	020	090	032
Compost + NPK 2-2	020	100	028
Compost + NPK 3-1	000	060	034
Compost + NPK 3-2	010	060	037

* value of below zero, and the real value of absorbance is (Absorbance ÷ 10,000), these values were obtained on 1 hour, 3 hours, and 5 hours warming up of the AA-680 spectrophotometer, respectively.

than for ordinary trace elements (Huheey et al., 1993).

The Ni contents in the forage were shown in detail in our other report (Kim et al., 2007), and it showed that the Ni contents of the sorghum hybrid (*Sorghum bicolor* (L.) Moench) ranged 6.3 ± 1.9 ~ 10.2 ± 3.6 ppm in a dry matter basis. Mengel and Kirkby (1978) wrote as follows; Normally the Ni content of plant material is about 0.1 ~ 5 ppm of the dry matter. Toxic symptoms in oats, a Ni sensitive crop, were observed in plants with Ni contents in excess of 100 ppm. But the uptake by less sensitive crops is lower.

And it is considered valuable to analyse Ni content in a more stable condition. Haraguchi (1993) cited that Ni had to adjust the standard solutions because the standard deviation reached twice after long time (3 hours), while the Cu was stable after the duration in Inductively Coupled Plasma (ICP) method. On the 3 hours warming time (Table 2) in our present experiment, because of unstable condition, the value of absorbance was -10 at 0 ppm standard solution, and only two standard solutions were used.

Baek and Zeong (1991) wrote that 28Ni has an orbital of $(3D^8 4S^2)$, while 29Cu has of $(3D^{10} 4S^1)$, and Ni had a different orbital with Cu. And it is considered that the different orbital of Ni might be a reason of a stronger bond energy than the Cu.

We think that the longer warming time of Ni and other metals is necessary for their better measuring; the reason might be the larger bonding energy of Ni. Bond energy of Ni-Ni, Cu-Cu, Mg-Mg, Ca-Ca, K_2 are 228.0, 190.4, 129, 105, 49.4 KJ/mol, respectively. (Huheey et al., 1993). And the standard oxidation potentials of a number of electrodes at 25℃ was different among the transition metals; $Fe \rightarrow Fe^{+2} + 2e$, $+0.440$ volt; $Co \rightarrow Co^{+2} + 2e$, $+0.277$; $Ni \rightarrow Ni^{+2} + 2e$, 0.250; $Cu \rightarrow Cu^{+2} + 2e$, -0.337. (Glasstone and Lewis, 1972)

Huheey et al. (1993) wrote the electron configurations, or distribution of electrons among orbitals, for the transition metals of the first series like this; when all of the energies are summed, including all of the electron-electron repulsions, it is found that the [argon(Ar)] $3d^n 4s^1$ configuration(24 Cr, [Ar] $3d^5 4s^1$; 29 Cu, [Ar] $3d^{10} 4s^1$) is lower in energy than the [Ar] $3d^{n-1} 4s^2$ configuration. That is: 21 Sc, [Ar] $3d^1 4s^2$; 22 Ti, [Ar] $3d^2 4s^2$; 23 V, [Ar] $3d^3 4s^2$; 25 Mn, [Ar] $3d^5 4s^2$; 26 Fe, [Ar] $3d^6 4s^2$; 27 Co, [Ar] $3d^7 4s^2$; 28 Ni, [Ar] $3d^8 4s^2$; 30 Zn, [Ar] $3d^{10} 4s^2$. Similarly, on polarograph the order was as follows; $Cu^{+2} < Cd^{+2} < Zn^{+2} < Mn^{+2}$. (Glasstone and Lewis, 1972)

Table 5 shows the effect of warming time on Cu analysis, range of background values for Ni, standard deviation(SD) of background, mean absorbance, SD of absorbances and the ratio of (mean / SD) of absorbance of Ni. The data were partly taken from Figures 1 2, and 3. And Cu analysis was carried out in our previous report (Choi et al., 2007). One hour warming up of the spectrophotometer the Cu result was good, and 3 or 5 hours data were not necessary.

With the increase of warming up time, the standard deviation (SD) of background values decreased from 21.5 to 11. And with the increase of the time $1 \rightarrow 3 \rightarrow 5$ hours warming up of the AA-680 spectrophotometer, (mean/SD) of absorbances of Ni observed increased $0.9 \rightarrow 2.5 \rightarrow 3.5$.

From Fig. 1, 2, 3 we conclude that as follows;

Table 5. Effect of warming time on Cu analysis, range of background values for Ni, standard deviation(SD) of background, mean absorbance, SD of absorbances and the ratio of (mean / SD) of absorbance of Ni

Species of Trace Metal	1 hour warming	3 hours warming	5 hours warming
Cu	good for the analysis	not necessary	not necessary
Range of background value for Ni (mean+SD) ~ (mean-SD)	(−27) ~ 16	2 ~ 48	800 ~ 822
SD of 22 background values for Ni	21.5	23	11
Mean of 22 absorbances of Ni observed	9.09	67.27	34.22
SD of 22 absorbances of Ni observed	9.21	26.75	9.53
(mean/SD) of absorbances of Ni observed	0.9	2.5	3.5

(7) It is necessary in Ni analysis warming up for longer period around 5 hours for this type of apparatus. And we think that the difference of warming time for Ni analysis in order to carry out better measuring; the reason might be the larger bonding energy of Ni than those of Cu, Ca, Mg and K. Similar to Ni, such transition elements as scandium(Sc), titanium(Ti), vanadium(V), manganese(Mn), iron(Fe), cobalt(Co), zinc(Zn), except chromium(Cr) and copper(Cu), may be difficult to analyse. And we would advise our method, with longer warming time around 5 hours of an atomic absorption spectro-photometer, in order to analyse these transition metals.

Ⅴ. ACKNOWLEDGEMENTS

ABSTRACT

Effect of Water Treatment Sludge (WTS) on trace metals content in Sorghum (*Sorghum bicolor* (L.) Moench) was investigated. At this report measuring of nickel (Ni) content of the forage was presented. Four treatments, Control, Compost, Alum + (nitrogen, phosphorus, potassium) (NPK), Compost + NPK, were applied to the

sorghum in a mountainous place near the Joongbu University. With the 1, 3, 5 hours conditions, the background value was the least on the 5 hours warming up of the AA-680 spectrophotometer, and on the condition (mean/ SD) of absorbances of Ni observed was the most. It is necessary in Ni analysis warming up for longer period around 5 hours for this type of apparatus. And we think that the difference of warming time for Ni analysis in order to carry out better measuring; the reason might be the larger bonding energy of Ni than those of Cu, calcium(Ca), magnesium(Mg) and (potassium) (K).

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