KRMIVA

DETERMINATION OF CHROMIUM IN THE FEED MIXTURES WITH ADDED Cr_2O_3

ODREĐIVANJE KROMA U KRMNIM SMJESAMA S DODATKOM Cr_2O_3

Vekoslava Stibilj, Jasna M. A. Stekar, Marinka Rodica

Original scientific paper - Izvorni znanstveni članak
UDC: 636.085.25
Received – promljeno: 25 November – studeni 1997.

SUMMARY

For the determination of digestibility we often decide to add an indicator, most frequently it is chromic (III) oxide. The method for chromium determination must give accurate and repeatable results. In our research chromium was determinated by atomic absorption spectrophotometry with a slightly modified Leaver's method. Each sample was analysed four times. In fifteen samples of feed mixtures for beef cattle, pigs, poultry and fish 0.0 g; 7.5 g and 10.0 g of Cr_2O_3 kg^{-1} were added. We think that the used method is suitable for chromium determination in feed mixtures with added Cr_2O_3. Our results were repeatable. The mean recoveries were 100.5% and 101.3% when 7.5 g and 10.0 g Cr_2O_3 were added. When 10.0 g of Cr_2O_3 were added, the values for P, Mg and Zn were lower than in the mixtures without an additive. The contents of Ca, K, Na and Mn were lower in some samples, while in the others they were higher than in samples without Cr_2O_3.

Key words: Determination, Chromic oxide, Feed mixtures

INTRODUCTION

Modern methods of energy evaluation in feed are still based on digestible nutrients. In vivo determination of digestibility is despite theoretically clear starting points a complicated, pretentious and expensive procedure, and we have to wait for the results quite a long time. In birds the determination of digestibility is even more complicated because faeces and urine are excreted together. Therefore researchers try to simplify the classic way of determining the digestibility by addition of indicators or markers to the feed. The digestibility for some components of the feed can be calculated from the consumed amount of indicator that has been excreted by faeces. The addition of indicators is suitable for ruminants, for animals with simple digestive tracts and for people. Schneider, 1935 established criteria for good indicators. Even though their number is enormous the chromic (III) oxide is primarily used. The determination of chromium in the biological samples is a pretentious analytical work. The method should give exact and repeatable results, and the recovery should be known.

THE AUTHORS DEDICATE THIS PAPER TO LATE PROF. DR. ZDRAVKO ČERNY, ZAGREB, CROATIA - OVAJ ČLANAK AUTORI POSVEĆUJU POKOJNOM PROF. DR. ZDRAVKO ČERNY, ZAGREB, HRVATSKA.

Dr. Vekoslava Stibilj, prof. dr. Jasna Stekar, Marinka Rodica, ing. kem., Univerza v Ljubljani, Biotehniška fakulteta, Oddelek za zootehniko, 1230 Domžale, Slovenija.

The objective of our work was to introduce a method of determination of chromium and to find out the effect of chromium on determination of essential micro and macro elements in feedstuffs.

MATERIAL AND METHODS

We prepared 15 samples of various feed mixtures; two were prepared for beef cattle, six for pigs, five for poultry and two for fishes. The samples were homogenised by use of mill Kladivar with 1mm sieve. Three groups of samples for analysis were prepared:

a) Feed mixtures without added Cr_2O_3

b) Feed mixtures with added 7.5 g Cr_2O_3 kg^{-1}

c) Feed mixtures with added 10.0 g Cr_2O_3 kg^{-1}

Chromium content in samples was determined with a slightly modified method as described in the book Herbage Intake Handbook Leaver, 1982.

Atter dry ashing of sample, the oxidation mixture of acids (H_3PO_4 + H_2SO_4) was added to the crude ash and heated till boiling at 280 °C - 290 °C, than 4.5% $KBrO_3$ was added and heating continued. When the solution became dark violet we continued to heat for 2 to 5 minutes. After cooling the solution, we diluted and determined the content of chromium by atomic absorption spectrophotometry.

Analyses were done in duplicate and two determinations were performed for each duplicate.

Table 1. Chromium recovery from different samples of feed mixtures with added Cr_2O_3*
Tablica 1. Očuvanje kroma iz raznih uzoraka krmnih smjesa kojima je dodan Cr_2O_3*

Feed mixture for Krmna smjesa za	No. of samples Broj uzoraka	7.5 g Cr_2O_3 kg^{-1} Mean ± s g Cr_2O_3 kg^{-1} Prosjek ± s g Cr_2O_3 kg^{-1}		10.0 g Cr_2O_3 kg^{-1} Mean ± s g Cr_2O_3 kg^{-1} Prosjek ± s g Cr_2O_3 kg^{-1}	
Beef cattle – Tovna goveda	1	7.64	0.06	10.73	0.20
	2	7.82	0.05	9.89	0.49
Mean ± s – Prosjek ± s		7.73 ± 0.11 (8)		9.99 ± 0.86 (8)	
Pigs – Svinje	3	7.23	0.05	9.80	0.18
	4	7.39	0.02	9.76	0.29
	5	7.31	0.30	9.72	0.19
	6	7.53	0.06	10.09	0.06
	7	7.60	0.42	9.51	0.12
	8	7.48	0.06	10.44	0.16
Mean ± s – Prosjek ± s		7.42 ± 0.23 (24)		9.88 ± 0.35 (24)	
Poultry – Perad	9	7.87	0.26	9.50	0.02
	10	7.59	0.11	10.76	0.05
	11	7.20	0.11	10.14	0.05
	12	8.52	0.04	10.23	0.38
	13	8.05	0.02	10.67	0.03
Mean ± s – Prosjek ± s		7.83 ± 0.47 (20)		10.26 ± 0.48 (20)	
Fish – Ribe	14	7.87	0.07	10.34	0.18
	15	8.05	0.03	10.31	0.05
Mean ± s – Prosjek ± s		7.95 ± 0.10 (8)		10.32 ± 0.12 (8)	

* Each sample was analysed four times – Svaki uzorak je analiziran četiri puta

() Number of determinations – Broj determiniranja

The standard solution with the 1 mg concentration of $Cr.ml^{-1}$ was prepared from $K_2Cr_2O_7$ by dissolving in distilled water. In each series of Cr determination in samples the content of Cr in Cr_2O_3 was determined.

The contents of Ca, P, Mg, K, Na, Mn and Zn in feed mixtures were determined by methods described in Metodenbuch, Band III., 1993.

RESULTS AND DISCUSSION

Chromium is one of the most extensively used external markers for digestibility determination in animals. Nutrient digestibility in animals is frequently estimated by using the indicator ratio technique with Cr_2O_3 as the indicator. Since these values are determined by the ratio of the concentrations of marker Cr in the diet and faeces, complete recovery and accurate estimation of this compound are essential. A small error in Cr determination, especially in the diet, causes a large discrepancy in the final calculation of digestibility. Despite this potential problem, the indicator ratio technique has long been used with ad hoc manipulations when complete faecal recovery of dietary Cr was not obtained (Saha and Gilbreath, 1991).

Table 2. Content of phosphorus, magnesium and zinc in diets without (0.0%) and with added Cr_2O_3 (0.75% and 1.0%)
Tablica 2. Sadržaj fosfora, magnezija i cinka u hrani bez (0.0%) i s dodatkom Cr_2O_3 (0.75% i 1.0%)

Feed mixture for	N*	P(g kg^{-1})			Mg (g kg^{-1})			Zn (g kg^{-1})		
Krmna smjesa za	Broj*	0%	0.75%	1.0%	0%	0.75%	1.0%	0%	0.75%	1.0%
		c_o	Δ	Δ	c_o	Δ	Δ	c_o	Δ	Δ
Beef cattle	1	4.6	-0.84	-0.81	2.8	-0.10	-0.30	63.9	+1.21	-10.23
Tovna goveda	2	8.8	-0.93	0.82	7.3	-0.26	-0.71	803.9	-113.7	-171.8
Pigs – Svinje	1	6.1	-1.05	-1.72	2.1	-0.20	-0.36	119.9	-26.16	-31.46
	2	6.2	-1.06	-1.21	2.3	-0.20	-0.30	243.0	-13.44	-1.27
	3	6.2	-0.47	-1.22	2.0	-0.15	-0.25	133.2	-3.03	-2.82
	4	6.5	-0.89	-0.83	2.0	+0.04	-0.16	100.0	-7.68	-12.14
	5	8.0	-0.90	-0.83	2.4	-0.35	-0.23	249.5	+16.54	-20.87
	6	8.9	-0.96	-0.86	2.3	-0.23	-0.08	256.0	-26.40	-50.09
Poultry – Perad	1	8.0	-0.82	-0.64	2.4	-0.20	-0.14	116.3	+6.92	-1.92
	2	5.1	-1.16	-1.00	2.5	-0.64	-0.96	106.7	-8.75	-7.91
	3	7.2	-0.27	-0.72	2.3	-0.05	-0.27	93.2	+30.07	-3.99
	4	6.5	-0.35	-0.86	2.6	-0.26	-0.41	1008.8	+15.50	-21.27
	5	5.0	-0.21	-0.26	2.6	-0.26	-0.17	83.6	-9.44	-17.67
Fish – Ribe	1	12.1	-0.26	-0.03	1.9	-0.02	-0.19	917.0	-0.30	-8.47
	2	13.0	+0.19	-0.20	2.0	-0.03	0.19	84.3	-10.07	-17.61

N*= number of samples – Broj uzoraka

$\Delta = c_o - c_d$, where – gdje je

c_o = element content in feed without added Cr_2O_3 – element u hrani bez dodatka Cr_2O_3

c_d = element content in feed with added Cr_2O_3 – element u hrani s dodatkom Cr_2O_3

Since variations in mineral content interfere with Cr determination (Williams et al., 1962., Green, 1975.), we investigated the impact of mineral variations in diet on analytical recovery of Cr.

To check the recovery of Cr from Cr_2O_3 itself and to validate the accuracy of the adopted method, several times (20) oven dried Cr_2O_3 was ashed and acid digested and analysed by the atomic absorption spectrophotometry. The chromium recovery was 102.0 ± 0.43% and it was in good agreement with literature data (101.0 ± 1.08%) (Saha and Gilbreath, 1991).

Table 1 shows the concentration of Cr in feed mixtures. It can be noticed that theoretical content and obtained results are in good agreement. The average chromium recovery for feed mixtures with 10.0 g Cr_2O_3/kg was 101.2 ± 0.4% and 100.5 ± 0.2% for diet with 7.5 g Cr_2O_3/kg. No differences were observed in recovery of Cr from diets with 0.75% and 1.0% Cr_2O_3. Certain authors reported that some cations increased or decreased the absorption of chromium. We have not observed that in our work.

We were interested in the influence of Cr on the determination of some cations in the samples of feed mixtures. Table 2 shows that lower values were obtained for P and Mg for both concentrations and for Zn at 10.0 g Cr_2O_3/kg^{-1} while some oscillations were observed for Na, K, Mn and Ca as shown in Table 3.

Table 3. Content of calcium, potassium, sodium and manganese diets without (0.0%) and with added Cr_2O_3 (0.75% and 1.0%)

Tablica 3. Sadržaj kalcija, kalija, natrija i mangana u hrani bez (0.0%) i s dodatkom Cr_2O_3 (0.75 i 1.0%)

Feed mixture for	N*	Ca (g kg^{-1})			K (g kg^{-1})			Na (g kg^{-1})			Mn (mg kg^{-1})		
Krmna smjesa	Br*	0%	0.75%	1.0%	0%	0.75%	1.0%	0%	0.75%	1.0%	0%	0.75%	1.0%
za		c_o	Δ	Δ	c_o	Δ	Δ	c_o	Δ	Δ	c_o	Δ	Δ
Beef cattle	1	12.5	+0.57	+0.26	7.6	-0.53	-0.25	2.0	-0.03	-0.09	87.3	-4.73	-13.46
Tovna goveda	2	37.5	-1.76	+0.69	17.3	-1.05	-0.24	10.8	-1.56	+0.13	520.8	-36.74	-65.02
Pigs – Svinje	1	7.3	+0.64	-0.84	6.4	-0.18	-0.30	2.2	+0.26	-0.05	70.4	-3.72	-7.91
	2	8.5	-0.94	-0.20	8.1	-0.65	-0.24	2.9	-0.02	+0.20	131.1	-31.66	-31.05
	3	8.3	+0.11	-0.80	7.3	-0.38	-0.12	2.3	+0.02	-0.06	81.8	-5.78	-7.26
	4	8.9	-0.71	-0.51	5.1	+0.41	+0.51	2.5	-0.37	-0.31	82.3	+9.35	+6.88
	5	10.2	-1.07	-0.94	6.9	-0.16	-0.25	2.6	-0.06	-0.11	147.2	-16.10	-14.60
	6	9.1	-0.05	-1.74	10.1	-0.87	-0.14	3.4	+0.21	-0.19	164.5	+40.18	-12.56
Poultry – Perad	1	12.7	-0.20	-1.40	8.9	+0.48	+0.59	1.8	+0.20	0.00	124.8	+17.25	-10.38
	2	24.9	+1.16	-0.30	6.5	+0.37	+0.20	1.6	-0.17	-0.02	125.1	-0.39	+0.18
	3	15.2	+1.05	-1.60	7.6	+0.03	-0.16	2.1	+0.21	-0.31	137.7	-8.12	-13.63
	4	16.2	-0.03	-2.18	8.1	+0.01	-0.11	1.9	+0.32	+0.07	115.1	-5.45	-9.87
	5	27.2	+0.59	-0.40	6.2	+0.83	+0.71	1.5	+0.04	-0.05	104.2	+3.33	+1.18
Fish – Ribe	1	21.8	-0.68	-1.55	6.0	+0.03	+0.16	5.0	+0.47	+0.07	64.9	-3.91	-4.03
	2	23.4	2.68	-2.67	6.0	+0,09	+1.27	5.5	+0.25	-0.76	63.8	-0.95	-8.52

N*= number of samples – Broj uzoraka

$\Delta = c_o - c_d$, where – gdje je

c_o=element content in feed without added Cr_2O_3 – Sadržaj elementa u hrani bez dodatka Cr_2O_3

c_d = element content in feed with added Cr_2O_3 – Sadržaj elementa u hrani s dodatkom Cr_2O_3

CONCLUSIONS

1. The atomic absorption spectrometry was used to determine Cr in 15 samples of various feed mixtures. All mixtures had 7.5 g and I 0.0 g Cr_2O_3 kg^{-1} respectively added beforehand.

2. We found the modified method as described by Leaver, 1982. suitable for the determination of chromium in feedstuffs with added Cr_2O_3. The obtained results were repeatable. The average chromium recovery was 100.5% and 101.3% in feed mixtures with 7.5 g and 10.0 g Cr_2O_3 kg^{-1} respectively.

3. The effects of added Cr_2O_3 on cations that were present in feed mixtures were the following:

– lower values were determined for P, Mg, and Zn in mixtures with 10.0 g Cr_2O_3 kg^{-1} than in mixtures without Cr_2O_3.

– in some samples of feed mixtures the contents of Ca, K, Na and Mn were lower while in the others they were higher than in samples without Cr_2O_3. Those deviations could be part of experimental error.

LITERATURE

1. Schneider, B. H. (1935): The subdivision of the metabolic nitrogen in the feces of the rat, swine and man. J. Biol. Chem. 109, 249.
2. Leaver, J. D. (1982): Herbage Intake Handbook. The British Grassland Society.
3. Methodenbuch, Band III, (1993): Die chemische Untersuchungen von Futtermitteln, Darmstadt, VDLUFA, Verlag.
4. Ajlec, R., M. Čop. J. Štupar, J. (1988): Interferences in the determination of chromium in plant material and soil samples by flame atomic absorption spectrometry. Analyst, 113 (4), 585-591.
5. Yanagisawa, M., M. Suzuki, T. Takeuuchi (1970): Cationic interferences in the atomic absorption spectrophotometry of chromium. Anal. Chim. Acta, 52, 386-389.
6. Saha, D. C., R. L. Glbreath (1991): Analytical recovery of chromium from diet and faeces determined by colorimetry and AAS. J. Sci. Food Agric., 55, 433-466.
7. Willliams, C. H., D. J. David, O. Iismaa (1962): The determination of chromic oxide in faeces samples by AAS. J. Agric.. Sci. 59, 381-385.
8. Green, H. C. (1975): The effect of valency state on the determination of chromium in perchloric acid media by AAS. Analyst, 10, 640-642.

SAŽETAK

Pri određivanju probavljivosti često se odlučuje za dodatak indikatora, najčešće krom (III) oksida. Metoda za određivanje kroma mora pružiti precizne i ponovljive rezultate. Krom je određivan atomskim apsorpcijskim spektrofotometrom prema donekle modificiranoj Leaverovoj metodi. Svaki uzorak analiziran je četiri puta. Krmnim smjesama za goveda u tovu, svinje, perad i ribe, ukupno 15 uzoraka, dodavano je 0,0 g, 7,5 g i 10,0 g Cr_2O_3 kg^{-1}. Smatra se da je upotrijebljena metoda prikladna za određivanje Cr u krmnim smjesama s dodatkom Cr_2O_3. Rezultati su bili ponovljivi. Prosječna iskoristivost iznosila je 100,5% i 101,3% kad je dodano 7,5 g i 10,0 g Cr_2O_3. Kad je dodano 10,0 g g Cr_2O_3 kg^{-1}, bile su niže vrijednosti P, Mg i Zn nego u krmnim smjesama bez dodatka. Sadržaj Ca, K, Na i Mn u nekim je krmnim smjesama bio manji, a u nekima veći nego u uzorcima bez Cr_2O_3.

Ključne riječi: Određivanje, Krom oksid, Krmne smjese