

THE SPECTROGRAPHIC ANALYSIS OF COMMERCIAL FEED STUFFS

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With the recent cooperative purchase and installation of a spectrographic laboratory by the State Chemical Laboratory and the University Department of Chemistry, several problems feasible for a joint research program were considered. Due to the tedious nature of the analyses required for the detection and quantitative estimation of added trace elements in commercial feedstuffs, it was felt that the development of a spectrographic procedure suitable for the simultaneous qualitative and quantitative determination of such added trace elements would be of considerable value to the State Chemical Laboratory.

Preliminary work has been limited to four elements: iron, manganese, copper, and cobalt. These elements are frequently added to commercial feedstuffs. A review of the literature indicated that while considerable work had been carried out with ashed biological samples, there was no mention of procedures suitable for the direct determination of these elements in feedstuffs. Nelson, Hamm, and Tsiang (1), O'Connor and Heinzelman (2), and Landon (3) have worked extensively with biological materials containing the above elements in trace amounts.

All spectograms were obtained with a Large Littrow (Bausch and Lomb) Spectograph on Eastman plates with a SA-1 emulsion. The plates were developed in the customary manner with Kodak Developer D-19 using an automatic Spec-Power plate processing unit.

QUALITATIVE ANALYSIS

A preliminary listing of possible lines for the four elements was made with the help of the Brode (4) tables. Several plates were exposed under different conditions of arcing, slit width, and plate position. Various electrode shapes were employed. Both feedstuffs and metallic salt samples were arced. An exhaustive study of the developed plates indicated that cupped anodes of 6 mm depth combined with flat cathodes (5/16 inch) were satisfactory. Plate position three coupled with a slit width of 10 microns when exposed for sixty seconds with an arc gap of 4-5 mm gave the best results. On the basis of further study the analysis lines shown in Table I were selected.

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TABLE I
QUALITATIVE ANALYSIS LINES

Element	Wave length of Line
Iron	2948.43-l
	2973.24-m
	2983.57-m
	3440.99-h
	4383.55-f
Manganese	2933.10-l
	2939.30-m
	2949.20-m
	3228.10-m
Copper	2997.40-vf
	3247.50-vh
	3724.00-vh
	4275.10-vf
Cobalt	3354.40-l
	3412.60-l
	3443.60-m
	3449.20-m
	3453.50-h
	3465.80-m

vh	very heavy	l	light
h	heavy	f	faint
m	medium	vf	very faint

A series of synthetic feed samples were prepared by the State Chemist. Maximum concentrations of analysis elements were: ferrous sulfate, 12mg/5gm sample; manganous chloride, 10mg/5gm sample; copper sulfate, 5mg/5gm sample; cobalt sulfate, 4mg/5gm sample. A silicic acid base was used. As can be seen from Table II, the method is well-adapted to the analysis of such feed samples for trace metals.

TABLE II
ANALYSIS OF SYNTHETIC FEED SAMPLES

Sample	Trace Elements Added	Trace Elements Found ¹
1	Cu, Co	Cu, Co
2	Mn, Co	Mn, Co
3	Fe, Co	Fe, Co
4	Mn, Cu	Mn, Cu
5	Fe, Cu	Fe, Cu
6	Fe, Mn	Fe, Mn
7	None added	None Found
8	Fe, Mn, Cu, Co	Fe, Mn, Cu, Co
9	Mn, Cu, Co	Mn, Cu, Co
10	Fe, Cu, Co	Fe, Cu, Co
11	Fe, Mn, Cu	Fe, Mn, Cu
12	Cu	Cu

¹Identification in each case made upon the basis of at least three analysis lines.

An unknown series of commercial feedstuffs was likewise obtained from the State Chemist; the results of these analyses are shown in Table III. Cobalt was found to be present in samples 1 and 4, even though not indicated on the analysis tag for the feeds. The presence of cobalt in these two samples was confirmed by chemical analysis.

TABLE III
ANALYSIS OF COMMERCIAL FEEDSTUFFS

Sample	Elements listed as added to feed	Elements found
1	Fe, Mn, Cu	Fe, Mn, Cu, Co ¹
2	Fe, Mn, Cu, Co	Fe, Mn, Cu, Co
3	Fe, Mn, Cu, Co	Fe, Mn, Cu, Co
4	Fe, Mn, Cu	Fe, Mn, Cu, Co ¹
5	Fe, Mn, Cu	Fe, Mn, Cu
6	Fe, Mn, Cu	Fe, Mn, Cu
7	Fe, Mn, Cu, Co	Fe, Mn, Cu, Co
8	Fe, Mn, Cu, Co	Fe, Mn, Cu, Co

¹Cobalt confirmed by chemical test

This method of qualitative analysis offers a considerable saving of time over the conventional wet methods of analysis. The ground sample is simply packed into the cupped anode and arced. No preliminary treatment is necessary.

QUANTITATIVE ANALYSIS

Preliminary work has indicated that raw, ground samples do not give sufficiently reproducible lines in the D. C. arc to allow their use for quantitative analysis. Emulsion calibration curves have been prepared with the aid of a logarithmic step-sector disc; line intensities being read with a modified Jarrel-Ash densitometer. Data has been treated according to the method of Churchill (5) with all plates having the same emulsion batch number.

Considerable work with ashed samples has indicated that either aluminum or molybdenum should serve as a suitable internal standard. Tests have indicated that the 3082.2 aluminum line should be suitable for comparison purposes. Suitable analysis lines appear to be: iron, 2790.1; manganese, 2949.2; copper, 3274.0; cobalt, 3499.2.

After considerable experimentation, the following procedure has been used:

Ash two gram sample of ground feedstuff; weigh ash, add an equal weight of 1% aluminum internal standard (silica base). Expose plate (SA-1) in position 4 with a current of 6 amperes and an exposure time of 60 seconds with an arc gap of 4-5 mm.

Typical results are shown in Table IV. The choice of analysis lines for copper and cobalt is evidently not satisfactory. Work is being con-

tinued to allow the choice of better analysis and comparison lines for these two elements.

TABLE IV
QUANTITATIVE ANALYSIS OF COMMERCIAL FEEDSTUFFS

Sample	% Elements listed	% Elements found
A. (11.70% ash)		
iron oxide	0.075	0.077
manganous sulfate	0.030	0.077
copper sulfate	0.003	0.002
cobalt sulfate	0.001	0.0002
B. (73.40% ash)		
iron oxide	1.0	1.027
manganous sulfate	0.104	0.095
copper sulfate	0.038	0.013
cobalt sulfate	0.015	0.002
C. (99.75% ash)		
iron oxide	-----	0.169
manganous sulfate	-----	0.110
copper sulfate	0.022	0.016
cobalt sulfate	-----	0.002

The quantitative method gives every indication of being capable of high accuracy. A further study of the conditions necessary for a rapid, accurate quantitative procedure is now being completed by means of a grant from the University Research Fund.

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