EDXRF APPLICATION NOTE

ANALYSIS OF ANIMAL FEEDS

#1279

SCOPE

The analysis of finished animal feeds and premixes is demonstrated using EDXRF with indirect excitation and Fundamental Parameters software, suitable for feeds for cattle, pigs, chickens, ducks, and other fowl and livestock.

BACKGROUND

The production and use of animal feeds is a global industry estimated in the hundreds of billions of dollars. Monitoring feeds and premixes is critical to ensure proper nutrient balance for the animal lifecycle, but also to ensure toxic metal constituents are below maximum concentration levels allowed by local regulations. While NIRS (near-infrared spectroscopy) is a widely accepted technique for the measurement of protein, amino acids, fat, oil, moisture, and fiber, it does not provide a complete solution. EDXRF (Energy-dispersive X-ray Fluorescence) is a simple, non-contact, *non-destructive* analysis technique that is ideal for use in the measurement of elemental concentration. EDXRF spectroscopy can be used for qualitative screening or feed characterization by elemental quantification. The method is useful in quantifying the elements that occur in finished feed formulations, as well as raw meals and premixes. Capable of measuring elements sodium through uranium, EDXRF can measure both elemental composition of the formulations and simultaneously screen for the presence of toxic metals such as chromium, lead, arsenic and cadmium. The Rigaku NEX CG analyzer meets this challenge by using secondary targets and polarization to remove background, thus allowing for the measurement of major, minor and trace elements in complex feed and premix formulations.

INSTRUMENTATION

Model:	Rigaku NEX CG
X-ray tube:	50 W Pd-anode
Excitation:	Indirect with polarization
Detector:	High performance SDD
Analysis Time:	100 sec – 10 minutes*
Environment:	Helium Purge
Standard:	15-position Sample Tray (32mm)
Options:	Manual Sample Press
	Light Element Optimization Target (LEO)*

* *Depending on application*

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SAMPLE PREPARATION

A sample is ground to a dry, homogeneous powder approximately 200 mesh (~75um particle size). Powder is placed in an XRF sample cup and compacted slightly using a Rigaku Manual Sample Press, to ensure even compaction of samples. Alternately, light element sensitivity can be optimized by using a hydraulic press to make a pressed pellet using 20 tons pressure for 30 seconds.

Manual Sample Press
For use with loose powder

31mm Pressed Pellet
For optimum LE performance

Sample preparation is fast and simple, giving the operator an efficient means of ensuring consistency in sample preparation, and important facet for achieving consistency of analytical performance.

RIGAKU RPF-SQX FUNDAMENTAL PARAMETERS (FP)

A Fundamental Parameters (FP) method was developed from Rigaku's RPF-SQX powder template. The Rigaku FP program automatically deconvolutes spectral peaks and models the sample matrix and X-ray absorption/enhancement effects using fundamental XRF equations. The versatile RPF-SQX software is simple to use and offers many ways to craft a matrix model based on the specific feed or premix type.

Information describing the part of the sample that XRF cannot measure (elements H-F) is entered into the template to model the balance of the matrix. In cases where there is only a single, known balance component, the software includes an extensive list of balance components, from a simple oxygen balance to more advanced compounds like cellulose and protein. The user can also easily define a new balance component if the feed balance is not listed in the template. For cases where there are more than one balance component, the Rigaku Scattering FP can be used. Scattering FP is an advanced method that uses the ratio of the Compton and Rayleigh scatter peaks to gain information on the average atomic number of the sample. This provides an estimate of the percentage of the sample that cannot be measured and yields more accurate analytical results for the remaining elements that can be measured, affording a semi-quantitative measurement of elemental concentrations without the need for a large suite of known assayed calibration standards.

In addition, a matrix-specific Matching Library can be easily created by the user using one or more assayed samples of the particular feed or premix type to further optimize the FP analytical results. The Matching Library is easy to create and is employed in conjunction with the standard FP library to optimize model of each matrix with multiple balance components so as to improve the calculation of concentration results.

The results shown here use various FP models to demonstrate these points.

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NEX CG RESULTS – FINISHED FEEDS

Scan of chicken feeds using 1000 sec analysis time and LEO target, loose compacted powder

Sample ID: Chicken Feed 1		Units: Mass%	
Component	NEX CG Value	Stat. Error	Est. LLD**
Na	0.432	0.0377	0.0657
Mg	0.258	0.0087	0.0035
Al	0.117	0.0018	0.0040
Si	0.307	0.0015	0.0029
P	0.548	0.0009	0.0012
S	0.303	0.0006	0.0006
Cl	0.362	0.0004	0.0004
K	1.15	0.0037	0.0008
Ca	0.845	0.0027	0.0015
Ti	0.0019	0.0001	0.0002
Cr	0.0004	0.0001	0.0001
Mn	0.0059	0.0002	0.0003
Fe	0.0545	0.0004	0.0001
Ni	0.0003	0.0001	0.0001
Cu	0.0262	0.0002	0.0001
Zn	0.192	0.0004	0.0001
Se	0.0001	0.0001	0.0001
Br	0.0006	0.0001	0.0001
Rb	0.0008	0.0001	0.0001
Sr	0.0013	0.0001	0.0001
I	ND*	--	0.0011

Sample ID: Chicken Feed 2		Units: Mass%	
Component	NEX CG Value	Stat. Error	Est. LLD**
Na	0.314	0.0984	0.2850
Mg	23.50	0.0994	0.0026
Al	0.252	0.0073	0.0192
Si	1.70	0.0073	0.0145
P	4.48	0.0049	0.0064
S	1.97	0.0027	0.0019
Cl	0.705	0.0013	0.0012
K	1.17	0.0064	0.0033
Ca	8.96	0.0150	0.0043
Ti	0.0229	0.0006	0.0010
Cr	0.0068	0.0002	0.0004
Mn	0.351	0.0018	0.0009
Fe	0.728	0.0019	0.0011
Ni	0.0035	0.0002	0.0003
Cu	0.134	0.0007	0.0003
Zn	0.393	0.0010	0.0003
Se	0.0032	0.0001	0.0001
Br	0.0016	0.0001	0.0001
Rb	0.0015	0.0001	0.0001
Sr	0.0074	0.0001	0.0001
I	0.0079	0.0006	0.0013

** ND means the component was not detected.*

****** *Estimated LLD numbers are based on current concentration levels and matrix makeup.*

Duck Feed – Comparison with ICP using 500 sec analysis time and LEO target, pressed pellets
In this example, Scattering FP is used in conjunction with a Matching Library created using assayed samples of the particular duck feed formulation.

Duck Feed	Mg	P	K	Ca	Mn	Fe	Cu	Zn	Na
Units	mass%	mass%	mass%	mass%	ppm	ppm	ppm	ppm	mass%
ICP	0.16	0.74	0.69	1.37	150	309	16	116	0.16
NEX CG	0.17	0.68	0.66	1.34	166	317	16	128	0.13

Note: If optimum sensitivity for Na and Mg is not required, the optional LEO target need not be used.

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NEX CG RESULTS – RAW MEALS and PREMIXES

Iron and Copper in Feed Raw Meals using 400 sec analysis time, loose compacted powder
Using oxygen balance component and Matching Library specific to the raw meal type.

	Sample A3		Sample A5		Sample AX1		Sample MX2	
Technique	ppm Fe	ppm Cu	ppm Fe	ppm Cu	ppm Fe	ppm Cu	ppm Fe	ppm Cu
ICP	41.0	13.5	52.2	13.0	38.5	12.6	21.5	1.7
NEX CG	**40.9**	**16.3**	**52.2**	**12.6**	**38.0**	**12.9**	**22.6**	**1.7**

Iron in Straw using 250 sec analysis time, loose compacted powder
Using scattering FP, no Matching Library.

	Sample 700
Technique	ppm Fe
ICP	31
NEX CG	**29**

Phosphorus in Premix using 250 sec analysis time, loose compacted powder
Using oxygen balance, no Matching Library.

	Sample 925	Sample 555	Sample 715
Technique	mass% P	mass% P	mass% P
ICP	0.523	0.503	0.531
NEX CG	**0.596**	**0.546**	**0.578**

The XRF results for P are very good using no matching library, within 15% relative of the ICP results. However, P compounds can be difficult to properly and fully digest, and analytical techniques that use digestion sample preparation may slightly underestimate the “true” P value due to incomplete digestion. XRF does not rely on digestion for sample preparation, and in this case may be closer to the “true” value for P without any corrections. If properly digested and assayed, a simple Matching Library can be easily built to match the XRF to ICP values. The following shows this principle, using a 1-point Matching Library based on sample 925.

Phosphorus in Premix using 250 sec analysis time, loose compacted powder
Using oxygen balance, with 1-point Matching Library particular to this premix type.

	Sample 555	Sample 715
Technique	mass% P	mass% P
ICP	0.503	0.531
NEX CG	**0.480**	**0.512**

Use of the Matching Library brings the XRF results for P to under 5% relative of the ICP values, excellent performance for fundamental parameters quantification.

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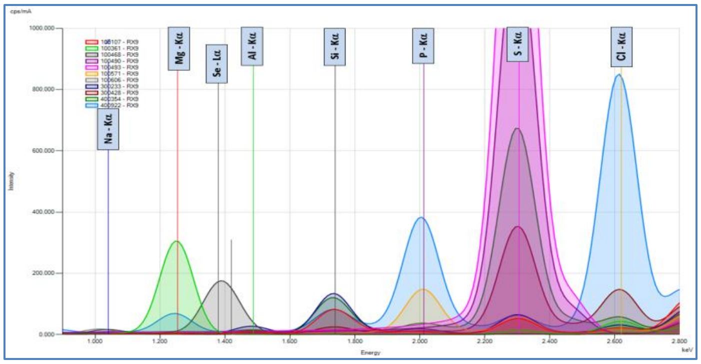
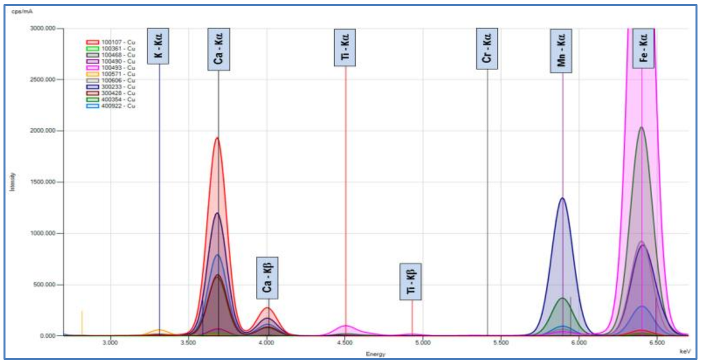
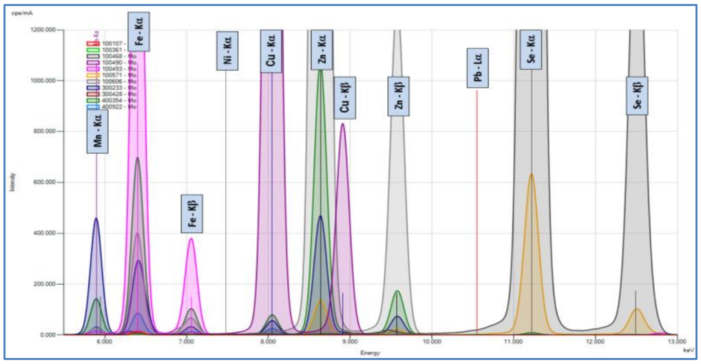
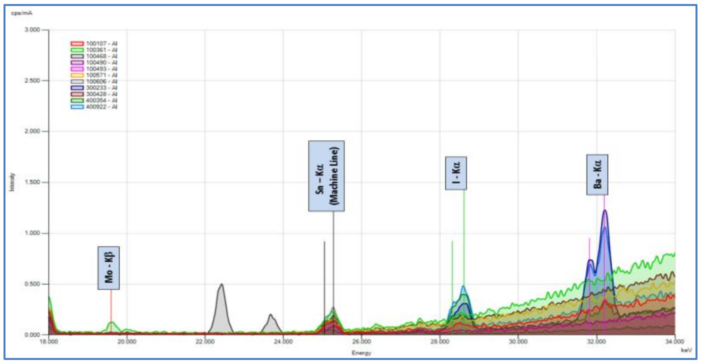
QUALITATIVE ANALYSIS

As an example of qualitative analysis, various feed spectra are shown.









TYPICAL DETECTION LIMITS

Typical detection limits are show here for common elements in finished feeds and premixes, where LLD indicates Lower Limit of Detection. Actual detection limits may vary and depend on sample type and elemental composition of the material, as well as analysis count times used.

Element of Interest	Typical Concentration Range (mass%)	Typical LLD Range (ppm)
Ca	0.0050 - 36.30	2 - 30
K	0.0120 - 2.10	3 - 35
P	0.0010 - 4.50	1 - 20
Fe	0.0020 - 23.20	1 - 5
Cu	0.0001 - 22.00	1 -5
Zn	0.0010 - 78.00	1 – 5
Mn	0.0004 - 61.20	1 - 6
Na	0.3000 - 20.90	250 - 3000
Mg	0.0600 - 46.90	15 - 1000
Co	0.0001 - 0.0010	1 - 2

Element of Interest	Typical Concentration Range (mass%)	Typical LLD Range (ppm)
Cl	0.0010 - 6.90	5 - 10
Se	0.0001 - 48.50	0.5 - 3
I	0.0010 - 0.0825	5 - 15
Cr	0.0002 - 0.0345	1 - 5
Ni	0.0001 - 0.0450	1 - 5
Si	0.0055 - 28.00	10 - 500
Mo	0.0000 - 0.0154	5 - 25
As	0.0000 - 0.0061	0.4 - 2
Sn	0.0047 - 0.0272	3 - 15
V	0.0000 - 0.0705	1 - 5

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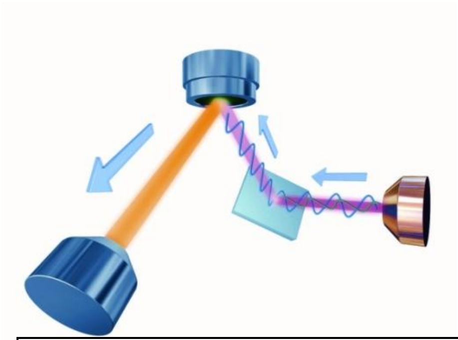
DISCUSSION



Secondary target schematic

The Rigaku NEX CG energy dispersive X-ray fluorescence (EDXRF) spectrometer combines indirect excitation with secondary targets and a polarization target, together with a high performance silicon drift detector (SDD) to give the operator a powerful and versatile analysis tool that is very simple to operate. Indirect excitation removes virtually all the background and thus affords spectra with a very high signal-to-noise ratio. This allows for much lower detection limits and is ideal for trace element measurement

While none of the samples tested contained toxic metals, indirect excitation lends itself well for trace measurement of such metals as Cr, Hg, Pb, As and Cd. Screening for the presence of toxic metals occurs at the stage of testing premixes and raw materials; toxic metal content is typically well below XRF analytical limits in finished feeds. The following shows typical detection limits for these toxic metals in animal feed products, depending on analysis time.

Element of Interest	Typical LLD Range (ppm)
Cr	1 - 3
Hg	1 -2
Pb	1 - 2
As	1 - 2
Cd	2 - 4

For less demanding applications within the animal feed industry, such as for daily quality screening of major elements in production QC processes, the NEX QC series of direct excitation analyzers also can be employed. These systems offer a smaller footprint and lower cost that is ideal for use at the production line.

There are many facets and applications within the feed industry that are served well by EDXRF. In general, FP returns results with an expected accuracy of 15-20% relative, and use of a well-crafted Matching Library improves FP accuracy to the order of 5-10% relative, which is ideal for screening of incoming materials, feed usage and feed manufacturing quality control.

CONCLUSION

The Rigaku NEX CG using the RPF-SQX Fundamental Parameters method yields excellent performance for the elemental analysis of various animal feed products. The use of RPF-SQX fundamental parameters eliminates the need for calibration standards. If desired, FP quantification can be optimized with Matching Libraries based on one or more assayed samples of the particular material type. These features make the NEX CG an ideal EDXRF tool for the elemental identification and characterization of animal feeds, raw meals and premixes throughout the animal feed industry to ensure proper nutrient balance and to screen for the presence of toxic elements.

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