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Chemical examination of feathers by an electron beam

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Abstract

Results are reported of the chemical examination of fourth primary feathers from Lesser Snow Geese (*Anser caerulescens*) by an electron beam from a scanning electron microscope. The microscope provided good resolution of chemical elements within the photon emission energy range extending from about 1.03 to 9.6 keV. Chemical elements measured included Na, Mg, Al, Si, S, Cl, K, Ca, Mn, Fe, Cr, and Zn. On a single sample basis only, a feather from a La Pérouse Bay colony goose could readily be distinguished from one from the Anderson River colony. A comparison of feather vane and shaft material confirmed the belief that vanes are more highly mineralized, and may contain a wider variety of chemical elements, than shafts. The microscope's main limitations are that it misses many chemical elements known to be present in higher energy ranges up to 40 keV and, since it primarily indicates surface chemicals it may not accurately reflect in-depth composition.

Résumé

L'auteur rapporte les résultats de l'examen chimique de quatre rémiges de petites oies blanches (*Anser caerulescens*), par balayage au train d'électrons émis d'un microscope électronique. Le microscope a permis une bonne résolution des éléments chimiques compris dans la gamme d'énergie photonique émise de 1.03 à 9.6 keV environ. On a ainsi mesuré notamment les éléments chimiques suivants: Na, Mg, Al, Si, S, Cl, K, Ca, Mn, Fe, Cr et Zn. Il a été possible, à partir d'un échantillon d'une unité seulement, de différencier facilement une plume provenant de la colonie d'oies de la baie de La Pérouse d'une autre en provenance de la colonie de la rivière Anderson. Une comparaison des barbes et des rachis (tiges) a permis de confirmer l'hypothèse que les barbes avaient une teneur en minéraux plus élevée et pouvaient comporter une plus grande variété d'éléments chimiques que les rachis. Les principales limitations du microscope viennent de ce que lui échappent maints éléments chimiques dont on connaît la présence dans les spectres d'énergie plus élevés, jusqu'à 40 keV, et de ce que, vu que son action réfléchissante s'exerce d'abord sur la couche superficielle, il est fort possible qu'il ne reflète pas fidèlement la composition chimique interne.

Introduction

In 1968 the Canadian Wildlife Service began testing the possibility of determining the origins of waterfowl through their feather chemistry. Major analytical tools used have been

various types of wet chemical analysis, particularly atomic absorption/flame emission spectroscopy, and X-ray fluorescing spectroscopy (Kelsall 1970, Kelsall and Calaprice 1972, Pannekoek *et al.* 1974). All have limitations and there has been a continuous appraisal of new and varied instrumentation.

We give here the results of a test analysis of feather material on a scanning electron microscope at the Pacific Biological Station of Environment Canada. That microscope has an X-ray detector and pulse height analyser as a peripheral device, thus permitting the electron beam to search out and identify, in their channels of emission energy, chemical elements in sample materials, as well as to provide the more conventional secondary electron image. We particularly wished to compare results obtained by electron beam analysis with those obtained from a CWS X-ray fluorescing spectrometer. The latter uses a 25 mCi Americium 241 source of irradiation, a lithium-drifted silicon detector with a resolution of about 200 eV, and has a useful analytical range (with some limitations) between about 2.3 and 40.0 keV in the K alpha emission energy range. It operates in air.

The electron beam has some advantages and disadvantages in the analysis of chemical elements. The main advantages are that a microscopic volume of material can be examined, and as this is done in a vacuum the resulting chemical spectra are nearly free of backscatter and other "garbage" peaks which invariably confuse results when radioactive materials are used as sources of irradiation (*i.e.* see Kelsall and Burton 1975). The instrument has an ultimate sensitivity of about 100 ppm for elements between sulfur and zirconium (about 2.3 to 15.8 keV). It is, therefore, not a particularly good instrument for identifying heavier elements.

The chief disadvantage is that the microscope only reflects the surface of any sample scanned. Unlike most other sources of radiation the electron beam does not penetrate deeply. It is a fine experimental tool for seeking chemical elements and developing procedures. It might not serve as a primary diagnostic tool for research in feather chemistry, our main interest (see Kelsall and Calaprice 1972), because it is virtually impossible to guarantee the complete removal of contaminants from the extremely complex surface of feathers. However, we wished to analyse some feather material to see if previously undetected elements might be found, and to provide at least a simple test of efficiency in comparing different materials.

Materials and methods

We examined three samples of feathers, all that time permitted. Table 1 summarizes the results. The complete computer output including plots of the data are retained by the CWS (see footnote 1), Delta. The data were derived from original computer programs developed at the Pacific Biological Station by Mulligan and Lapi.

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The samples were as follows: a portion of the vane from a fourth primary feather of a Lesser Snow Goose from the Anderson River Delta, a comparable portion of vane from a feather of a Lesser Snow Goose from La Pérouse Bay, and a portion of shaft from the same feather from La Pérouse Bay. They were introduced to the microscope's vacuum chamber on conventional plug mounts.

The samples were cleaned before examination by methods described by Pannekoek *et al.* 1974.

Results

The electron beam is not as sensitive above about 9 keV as CWS X-ray equipment. Hence, the electron beam results do not show such elements as bromine, iodine, and barium which we know are present in feathers. On the other hand it is much more sensitive than CWS equipment at energies below approximately 2.3 keV. Sulfur, in very large quantities (over 10,000 ppm in feathers), is the lowest element on the energy emission scale which is normally detected by CWS equipment. Table 1 shows, however, that the electron microscope has picked up silicon, aluminum, magnesium and sodium, extending its range down to 1.04 keV. In this particular case the specific values for aluminum, and to a lesser degree those for silicon, are not entirely reliable since these two elements are included in parts of the particular specimen chamber used.

Our main interest was to see whether or not the equipment would identify elements of which we were previously unaware. Sodium, magnesium, aluminum and silicon are all below the limits of detection with the CWS X-ray equipment, but their presence was known from wet chemical methods of analysis (Kelsall 1970). Chlorine had not been certainly identified with the X-ray equipment. The shaft of the feather sample from La Pérouse Bay shows the element chromium. The presence of that element was known from other work (Kelsall 1970), but it had been masked by backscatter and electronic effects in the X-ray analyses.

The relative mineralization of the vane and shaft portions of the feather from La Pérouse Bay is also of interest. From results by Hanson and Jones (1968), it has long been thought that shafts were less mineralized than vanes. Our results bear this out. The analyses show K alpha peaks for seven elements common to both the vane and shaft samples (Table 1). In five of these (Mg, Si, S, K and Ca) the greatest concentration is found in the vane and in one case (Fe) differences are negligible. The shaft appears to contain approximately twice the concentration of aluminum found in the vane. It must be recognized, here and elsewhere, that extensive conclusions are not warranted on the basis of single sample comparisons, but they do provide useful indications of what is probably the case.

Comparisons of the vane samples from Anderson River and La Pérouse Bay are of great interest. Chlorine is present only in the Anderson River sample and copper only in the La Pérouse Bay sample. This reawakens our long held hope that some goose colonies might be identifiable on a single element basis, but much further testing is necessary. Sodium is also present only in the Anderson River sample but this may not be significant since that element is at the extreme low end of the detection range of the electron microscope. Potassium is

seemingly about 10 times as abundant in the La Pérouse Bay sample as in the other two samples.

Discussion

The electron beam gives results comparable in clarity to those which might be expected using an X-ray tube source of excitation in a vacuum. For that reason alone these results are interesting. An efficient tube source would provide a spectrum over approximately the same range of elements, but with careful construction and a secondary target of silver it might be possible to identify elements above zinc on the emission energy scale, from their L and M emission energies. Hopefully these elements would include bromine, which we know is present, and possibly arsenic, selenium and others. Thus 16, and possibly more, elements would be available for use as diagnostic variables.

References

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Table 1

The results of examination of feather material from Lesser Snow Geese in an electron beam. The emission energy indicates the central point in spectral peaks to which curves were fitted. The penultimate column gives the element involved and the ultimate column the area under each peak in terms of electron counts

Source of sample	Energy (keV)	Energy error	Peak to background height ratio	Element classification	Normalized area
Anderson River - vane	1.0379	0.00421	0.1449	Na Ka	5,267
	1.2579	0.00189	0.3235	Mg Ka	13,287
	1.4823	0.00053	1.3358	Al Ka	64,995
	1.7309	0.00147	0.4084	Si Ka	27,358
	2.3040	0.00013	6.5476	S Ka	376,298
	2.4597	0.00000	0.4169	S Kβ	23,807
	2.6184	0.00120	0.5141	Cl Ka	27,568
	3.3155	0.00189	0.2855	K Ka	11,371
	3.6841	0.00031	2.5616	Ca Ka	98,212
	4.0047	0.00175	0.3491	Ca Kβ	11,967
	5.8923	0.02330	0.0396	Mn Ka	955
	6.3934	0.00610	0.1376	Fe Ka	2,567
	8.6063	0.00695	0.1638	Zn Ka	2,230
La Pérouse Bay - vane	1.2569	0.00242	0.2906	Mg Ka	13,920
	1.4819	0.00060	1.1095	Al Ka	50,001
	1.7304	0.00170	0.3259	Si Ka	21,645
	2.3034	0.00014	6.6863	S Ka	343,878
	2.4609	0.00180	0.4837	S Kβ	24,053
	3.3351	0.01334	0.0341	K Ka	1,307
	3.6852	0.00021	3.4801	Ca Ka	119,527
	4.0057	0.00116	0.4798	Ca Kβ	15,141
	5.8461	0.02441	0.0270	Mn Ka	589
	6.3941	0.00902	0.9550	Fe Ka	1,571
	7.9931	0.03780	0.0296	Cu Ka	441
	8.5950	0.00674	0.1358	Zn Ka	1,651
	9.6015	0.04949	0.0225	Zn Kβ	269
La Pérouse Bay - shaft	1.2666	0.00239	0.1764	Mg Ka	5,808
	1.4813	0.00018	3.0514	Al Ka	110,502
	1.7800	0.00147	0.2836	Si Ka	14,058
	2.3059	0.00012	4.5177	S Ka	194,052
	2.4597	0.00000	0.3569	S Kβ	13,367
	2.6162	0.00308	0.1493	Cl Ka	5,242
	3.3111	0.01464	0.0288	K Ka	815
	3.6856	0.00077	0.6464	Ca Ka	15,998
	4.0049	0.00448	0.0965	Ca Kβ	1,870
	5.4169	0.02145	0.0283	Cr Ka	500
	6.3861	0.00478	0.1268	Fe Ka	1,569

