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Comparison of neutron activation analysis with conventional detection techniques for the evaluation of trace elemental contamination in Mallard (*Anas platyrhynchos*) feathers

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Abstract Instrumental neutron activation analysis (INAA) was used to determine trace elemental contamination in bird feathers. Primary feathers from twelve mallard (*Anas platyrhynchos*) ducks, migrating through the Thousand Islands region of Ontario, Canada, were analyzed for selenium, mercury, chromium, arsenic and antimony. Certified reference materials were used to assess the quality of the analytical procedure. Quantification of chemical elements was performed using Ortec Gamma Vision software. Five chemical elements were quantified, with corresponding analytical uncertainties of less than 20%. Results indicated the presence of As (max = 0.13 mg kg^{-1}), Cr (max = 2.6 mg kg^{-1}), Hg (max = 7.7 mg kg^{-1}), Sb (max = 0.31 mg kg^{-1}) and Se (max = 1.31 mg kg^{-1}). To assess the validity of using INAA as a quantitative analytical technique for feather samples, two standard reference materials were examined and mercury results were compared to those obtained from both direct mercury analysis (DMA) and cold vapour atomic absorption spectroscopy (CVAAS). Several CVAAS results differed significantly from the INAA results; in many instances CVAAS appeared to under-report when compared to INAA, with relative percent difference values as high as 126%. Conversely, results obtained using DMA compared favourably with INAA. For all samples, RPD values were within 30%. This is the first study to use INAA to examine feather contamination in Canadian migratory waterfowl and the first to corroborate INAA feather results by comparing them to those obtained using CVAAS and DMA.

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Introduction

The Mallard is the best known wild duck in the world, with significant populations existing in North America, Europe and Asia [1]. Mallards are found throughout Canada and the United States; during the summer months Mallards can be found as far north as Alaska and the northern Northwest Territories, and in colder months, the majority migrate to the central and southern United States where lakes and ponds remain free of ice all year round. However, despite the cooler temperatures, many regularly choose to winter in Southern Ontario [1, 2]. In addition to being easily recognizable, Mallards are also one of the most popular game birds as a result of the ease with which they can be attracted to decoys and the excellent quality of their flesh. No duck is more extensively hunted: in Canada, it is estimated that greater than 50% of all duck kills are Mallards [1]. Given this, it is important to monitor contamination levels in these birds in order to protect individuals who consume significant quantities of their tissue throughout the year.

Historically, contaminant exposure was determined primarily by killing and therefore based on organ analysis [3]. Although kill studies are still common, many sampling efforts are now turning to the use of investigative techniques using non-lethal matrices such as feathers [4]. Feathers are useful indicators of elemental exposure as they provide insight into the overall body burden at the time of formation [5]; elemental accumulation in the feathers takes place throughout feather growth [6, 7]. Once the feathers are fully formed, the attached blood vessels atrophy and the

feather becomes physiologically separated from the bird, effectively halting any further transport of contaminants to them [8]. The use of feathers in biomonitoring activities is also attractive because samples are easy to collect non-invasively and to store indefinitely.

The selection of an appropriate analytical technique is an essential component of every successful environmental study. However, the task is not always an easy one as researchers are seemingly endlessly confronted with sample matrices containing varying degrees of complexity and homogeneity with respect to contaminant distribution. Several analytical techniques have been used to determine elemental concentrations in bird feathers, some of which include flame, graphite furnace and cold vapour atomic absorption spectroscopy (FAAS, GFAAS, CVAAS), inductively coupled plasma-mass spectrometry (ICP-MS), direct mercury analysis (DMA) and instrumental neutron activation analysis (INAA). Of these, CVAAS is used almost exclusively for mercury determinations while GFAAS and ICP-MS are typically used to evaluate most other elements. Despite the fact that INAA has been successfully validated for the chemical characterization of several biological and geological samples [9–12], few studies have used INAA to examine bird feathers [5, 9, 13–17]. Instrumental neutron activation analysis provides an attractive alternative to traditional analytical techniques as it requires very little sample preparation, is non-destructive in nature and is largely unaffected by the sample matrix.

In the present work, neutron activation analysis is examined as a quantitative, non-destructive detection technique for the evaluation of mercury, selenium, arsenic, chromium and antimony in Mallard feathers. Values obtained via NAA are compared against those collected using more conventional techniques such as cold vapour atomic absorption spectroscopy and direct mercury analysis.

Experimental

Reagents and materials

Nitric acid (mass fraction purity 0.67–0.70, trace metal grade), sodium chloride, tin (II) chloride (technical grade), hydrochloric acid (mass fraction purity 0.34–0.37, trace metal grade) and nitric acid (Optima) were obtained from Fisher Scientific. Potassium permanganate (low Hg), potassium persulfate (mass fraction purity 0.99, A.C.S. reagent grade), hydroxylamine sulfate, sodium borohydride (mass fraction purity $\geq$0.98) and sodium hydroxide (mass fraction purity >0.97, A.C.S. reagent grade) were purchased from Sigma–Aldrich. Double deionized water (17.8 MΩ) was prepared using an E-Pure™ Water Purification System, Barnstead International. Whirl–Pak® bags were obtained from Cole-Parmer.

Analytical reference standards for selenium, mercury, antimony, chromium and arsenic were purchased from SCP Science (Baie-d'Urfe, QC, Canada) and Transition Technologies (Toronto, ON, Canada). Tantalum standards were acquired from Inorganic Ventures (Lakewood, NJ, USA).

Sample collection and preparation

Feather samples were collected, under a Scientific Collection Permit issued by the Canadian Wildlife Service, between October 2009 and January 2010 from Mallard ducks (*Anas platyrhynchos*) migrating through the 1000 Islands region of the Great Lakes, just offshore of Kingston, Ontario, Canada. Primary feathers were plucked from both wings of each bird, transferred to Whirl–Pak® bags and stored at room temperature until analysis. Just prior to analysis, each feather was separated into vane and rachis (stem) portions.

Instrumental neutron activation analysis

Samples weighing between 0.05 and 0.42 g were packed into polyethylene vials for neutron irradiation. Vane and rachis portions were analyzed separately. Blank vials were also irradiated to account for background contamination. Certified reference materials, NRC PACS-2 and NIST 2711, were prepared similarly and analyzed for quality control purposes. All samples and certified reference materials analyzed for arsenic, antimony, chromium and mercury were irradiated at a neutron flux of 5×10^{11} cm^{-2} s^{-1} for approximately 18 h in the SLOWPOKE-2 nuclear reactor facility at the Royal Military College of Canada, Kingston, Ontario; samples analysed for selenium content were irradiated for only 18 s. Minimum decay and count times were 3.9 days and 3.5 h, respectively. Nuclear data for the elements used in this study can be found in Table 1. After appropriate cooling, the gamma activities of the irradiated samples were measured with a Ortec Pop-top High Purity Germanium (HPGe) gamma-ray spectrometry system, equipped with a co-axial GMX detector located behind a 0.5 mm beryllium window, operating at 40% efficiency at the 1332 keV photopeak of ^{60}Co (GMX 40 P4-70-S, EG & G Ortec, Oakridge, TN,

Table 1 Nuclear data for the nuclides utilized in this research

Element	Activated nuclide studied	Half-life	Gamma-ray used for quantification (keV)
As	^{76}As	26.32 h	559.1
Cr	^{51}Cr	667.2 h	320.08
Hg	^{197}Hg	65 h	77.6
Sb	^{122}Sb	65.28 h	564.1
Se	^{77m}Se	18 s	161.9

USA). Data acquisition and analysis were performed using Ortec Gamma Vision 6.08 software.

Direct mercury analysis

Feather-mercury concentrations were assessed using a direct mercury analyzer, Milestone DMA-80 (ATS scientific Inc., Burlington, ON, Canada). A standard calibration curve was automatically generated from standards containing 1, 5, 10, 20, 30, 50, 200 and 400 ng of mercury. Mercury concentrations in the samples were calculated from the recorded signal using the calibration curve. Samples weighing between 3 and 180 mg were weighed directly into 1.5 cm^3 quartz weigh boats and then loaded onto the DMA-80 autosampler. Two certified reference materials were used to confirm instrument calibration and method validity; Tort-2 and Mess-3 were both obtained from the National Research Council of Canada for this purpose. A blank sample was analyzed first to determine a baseline reading. Additionally, blank samples were analyzed between each feather sample to ensure against cross-over contamination. Duplicate analyses were performed for ten of the samples for precision purposes. Data acquisition and analysis were performed using EasyDOC 2.0 software.

Cold vapour atomic absorption spectroscopy

Feather-mercury concentrations were also analyzed using a cold vapour–flow injection mercury system, FIMS^{TM}-100 (PerkinElmer, Waltham, MA, USA) equipped with an AS-90 autosampler. Calibration standards (2.0, 8.0 and 16.0 ng cm^{-3}), a control sample (NIST 2702), a blank and all feather samples were transferred to Teflon microwavable vessels, MARS Xpress (CEM Corporation, Matthews, NC, USA), and digested in a solution of 4 cm^3 nitric acid (trace metal grade), 1 cm^3 0.05 (m/v) potassium permanganate solution, 1 cm^3 0.05 (m/v) potassium persulfate solution and 5 cm^3 distilled deionized water using a microwave accelerated reaction system, MARS (CEM Corporation, Matthews, NC, USA). Post digestion, extraction volumes were made up to 25 cm^3 with distilled deionized water. Data acquisition and analysis were performed using WinLab32 for AA^{TM} software.

Results and discussion

Analysis of certified reference materials by INAA

An important step in evaluating the applicability of a particular analytical technique for use in the assessment of a new sample matrix involves the analysis of certified reference materials. Ideally, a reference material of the desired matrix would be chosen. However, if none is available a suitable alternative must be found. In the case of feathers, there exists no reference material for comparison purposes. As a result, NIST 2711 (Montana soil) and NRC PACS-2 (Marine sediment) were selected for this study. Table 2 shows the obtained and certified values for each element studied as well as the corresponding percent recoveries and relative standard deviations. Values for As, Cr, Hg and Sb, are within 20% of the certified values and relative standard deviation values were all better than 5%, indicating satisfactory performance of INAA for the determination of these elements in the reference samples. Selenium recovery in PACS-2 was within 20% of its target; however the associated relative standard deviation was high at just under 40%. Whilst the higher relative error for selenium is less than desirable, the finding is not entirely surprising as elevated error measurements for this element have been previously reported [9]. In the case of NIST 2711, selenium recovery was found to be 240% of the target value. When examined for possible interferences, it was found that this particular reference material contains measurable and significant

Table 2 Obtained and certified values for the analyzed reference materials

Element		NIST 2711—Montana soil			NRC PACS-2—Marine sediment		
		Obtained	Certified	% recovery	Obtained	Certified	% recovery
As	mg kg^{-1}	99.8	105	100	26.1	26.2	95
	RSD/%	0.2	7.62		0.4	5.73	
Cr	mg kg^{-1}	54.7	52.3	105	97	90.7	116
	RSD/%	0.7	–		1.0	5.07	
Hg	mg kg^{-1}	6.7	6.25	118	3.6	3.04	107
	RSD/%	1.5	3.04		2.8	6.58	
Sb	mg kg^{-1}	19.7	19.4	104	11.8	11.3	102
	RSD/%	0.5	0.52		0.8	23.00	
Se	mg kg^{-1}	1.3[a]	1.52	86	0.95	0.92	103
	RSD/%	7.7	9.21		36.8	23.9	

[a] Concentration corrected for tantalum background

Table 3 Mallard characteristics and chemical elements determined by INAA in the rachis (R) and vane (V) portions of feathers collected from migratory waterfowl in Canada's Thousand Islands region

Trait		Mallard																							
		1		2		3		4		5		6		7		8		9		10		11		12	
Sex	M/F	M		M		M		F		F		M		F		M		F		F		F		M	
Mass	/kg	1.36		1.36		1.25		1.13		1.02		1.47		1.25		1.70		1.13		1.13		1.02		1.59	
Length	/cm	49		47		49		50		43		52		46		53		46		48		45		51	
Wingspan	/cm	76		84		80		80		74		92		80		90		80		78		78		96	
Element		R	V	R	V	R	V	R	V	R	V	R	V	R	V	R	V	R	V	R	V	R	V	R	V
As	mg kg^{-1}	0.016	0.067	0.2	0.13	0.22	0.15	0.031	0.041	0.039	0.095	0.11	0.07	nd[a]	0.05	0.07	0.06	0.026	0.08	0.085	0.08	0.032	0.10	0.045	0.05
	RSD/%	4	44	8	5	7	5	17	13	7	10	29	9	–	40	13	29	19	13	8	13	19	10	18	40
Cr	mg kg^{-1}	1.1	1.8	0.6	2.1	0.5	3.1	0.2	0.85	0.18	1.6	0.1	1.4	nd	2.1	0.25	2.6	nd	1.7	nd	4.9	nd	1.6	0.12	1.3
	RSD/%	9	6	33	10	20	6	15	8	33	19	40	14	–	14	18	12	–	14	–	4	–	6	33	8
Hg	mg kg^{-1}	0.23	0.57	0.90	2.2	0.40	1.0	0.15	0.33	1.6	2.7	0.86	1.0	3.5	7.7	0.27	0.81	0.13	0.29	0.15	0.34	0.04	0.16	0.31	0.50
	RSD/%	3	1	1	0.5	3	10	7	3	6	4	1	10	3	1	4	1	8	7	7	3	16	6	3	2
Sb	mg kg^{-1}	0.007	0.077	0.12	0.083	0.008	0.20	0.016	0.12	0.025	0.58	0.010	0.18	0.028	0.31	0.009	0.067	0.010	0.12	0.034	0.52	0.022	0.19	0.018	0.11
	RSD/%	14	1	8	1	25	5	6	8	4	2	10	6	11	3	11	3	20	8	6	2	5	5	6	9
Se	mg kg^{-1}	0.44	0.95	0.76	1.3	0.33	0.8	0.39	0.58	0.51	0.9	0.69	1.0	0.57	1.0	0.39	1.0	0.32	0.63	0.77	1.1	0.42	1.1	0.48	1.1
	RSD/%	9	7	8	5	12	13	10	12	10	22	9	20	9	10	13	10	13	14	8	9	10	8	9	8

nd not detected, sample concentration below method detection limit

quantities of tantalum—the presence of which can sometimes make selenium analysis more challenging as the ^{182}Ta 264-keV peak interferes with the 265-keV peak of selenium [18]. Fortunately, tantalum also has a gamma ray peak at 222 keV that is free of interference so long as sufficient time is allowed for bromine to decay; in this study, NIST 2711 was counted after 35 days. By using the ratio of counts at 264 keV and 222 keV, the Ta contribution to the Se peak at 265 keV can be determined. This value can then be subtracted from the ^{75}Se 265-keV peak to get the true value for selenium. In practice, the interference derived from tantalum is likely to be less relevant in feathers than in soil. When this technique was applied to NIST 2711, the analyzed concentration fell within 20% of the certified value (RSD = 7.7%), indicating satisfactory performance. In 2006, Figueiredo et al. [10] reported on the successful determination of As, Cr, Sb and Se in five other environmental certified reference materials, Fish Tissue (IAEA-407), Seafood Material (*Almeja Venus Antiqua*, MR-CCHEN-002), Tea Leaves (INCT-TL-1), Mixed Polish Herbs (INCT-MPH-2) and Marine Sediment (IAEA-433) by INAA. And in early 2010, França [9] reported on the successful evaluation of Cr, Hg, Sb and Se in two biological certified reference materials, Hay Powder (IAEA V-10) and Lichen (IAEA-336) using k_0-INAA. Given the results from the present study, along with those from others' previous studies, confidence exists in the ability to analyze for and quantify trace elemental contamination in avian feathers through the use of instrumental neutron activation analysis.

INAA Mallard feather analysis

The primary feathers from twelve Mallard ducks were separated into rachis and vane portions, packed into 2 cm^3-polyethylene vials and analyzed via INAA for antimony, arsenic, chromium, mercury and selenium. Table 3 shows the results from this analysis along with the associated relative standard deviations. Concentrations in the rachis ranged from 0.016 to 0.22 μg g^{-1} for arsenic, 0.1 to 1.1 μg g^{-1} for chromium, 0.04 to 3.5 μg g^{-1} for mercury, 0.007 to 0.12 μg g^{-1} for antimony and 0.32 to 0.77 μg g^{-1} for selenium, whilst vane concentrations ranged from 0.041 to 0.15 μg g^{-1} for arsenic, 0.85 to 4.9 μg g^{-1} for chromium, 0.16 to 7.7 μg g^{-1} for mercury, 0.067 to 0.58 μg g^{-1} for antimony and 0.58 to 1.3 μg g^{-1} for selenium. Corrective calculations were not required for selenium as no detectible quantities of tantalum were observed. Elevated levels of mercury and chromium were detected in the feathers, indicating a need for further studies of metal distribution in Mallards, particularly since they are one of the most popular game birds in the area.

Rachis and vane portions of the feather were examined to determine where in the feathers the contamination is sequestered and to evaluate the existence of any correlations between element concentrations in each portion. For all elements, save arsenic, contamination was concentrated in the vane portion of the feather. For arsenic, the results were more variable; in seven of the samples the majority of the arsenic was found in the vane, whereas in the other five samples more arsenic was found in the rachis. Variations and irregularities in different feather parts have been previously reported [16]. However, the cause of the variations is unclear. In order to determine whether or not there was a relationship between concentration levels in the different portions, a Pearson's coefficient of correlation was calculated for each element. A strong correlation was found for arsenic (r = 0.79), chromium (r = 0.62), mercury (r = 0.99) and selenium (r = 0.69). The near perfect correlation between the amount of mercury found in the vane portion and the amount found in the rachis has also been noted by Goede and de Bruin [15]. Conversely, there did not appear to be any relationship (r = −0.01) between antimony concentrations in the two components.

Correlations between elements found in the feathers were also examined. Results are shown in Table 4. Moderate correlations were found to exist between arsenic and chromium (r = 0.43), mercury and antimony (r = 0.30) and antimony and chromium (r = −0.30). The correlations between the remaining elements were less than 25% in all instances and in some cases were less than 10%. The magnitude of correlation between the elements speaks to the diversity of Mallard summer breeding locations; individuals exposed to the same environmental conditions and food sources would be expected to display strong inter-element correlations. Therefore, given the low to moderate correlations demonstrated in this study, it is reasonable to suggest that Mallards migrating through south-eastern Ontario are originating from a number of different breeding grounds.

Comparison of INAA mercury with DMA and CVAAS

Although several standard reference materials have been successfully analyzed via INAA, it is difficult to know whether successes with one matrix will directly transfer

Table 4 Pearson's coefficient of correlation (r)[a] between elements detected in feather sample vanes

Element	Se	Sb	As	Cr
Hg	0.17	0.30	−0.11	−0.16
Se		0.06	0.22	0.08
Sb			0.10	−0.30
As				0.43

[a] $r = \frac{\sum x_i y_i - n\overline{xy}}{(n-1)s_x s_y}$

into successes with an entirely different matrix. In some instances, the successful analysis of reference materials has lead to erroneous conclusions about the selection of a particular method for mercury determinations [19]. Given that there does not exist a certified reference material for feathers, it is prudent to compare INAA findings against those obtained using more traditional techniques in order to perform a complete assessment with regard to whether or not INAA is a suitable analytical technique for trace contamination in this matrix.

Mercury was chosen as the test element for technique comparison. The two techniques chosen to compare INAA against were cold vapour atomic absorption spectrometry (CVAAS) and direct mercury analysis (DMA). The use of CVAAS for environmental samples is routine in many laboratories and has been used extensively for the analysis of biological samples [17, 20–38], whereas DMA is used far less often [39]. Indeed, CVAAS is one of the most common analytical techniques used for the determination of mercury in biological samples due to its high sensitivity

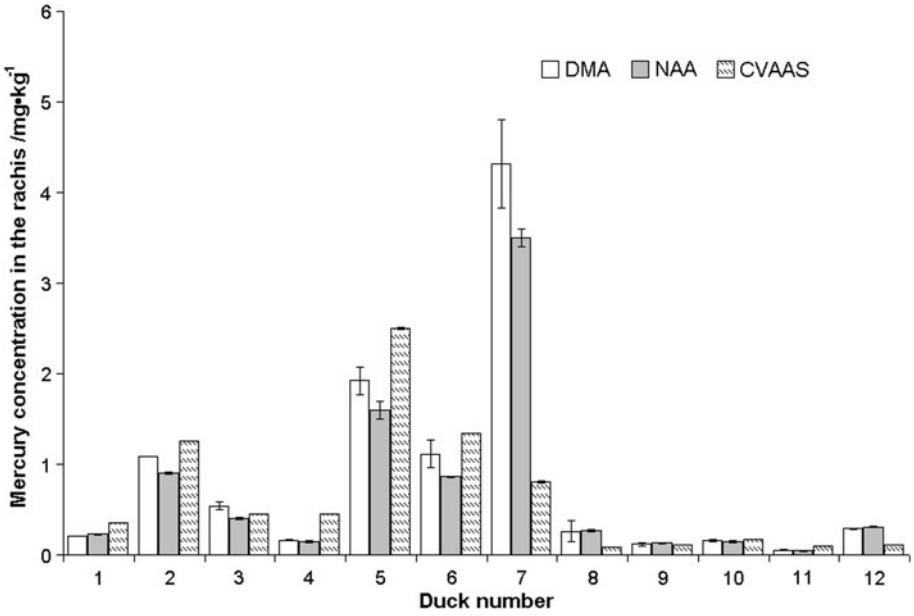

Fig. 1 Comparison of rachis-mercury concentrations for DMA, NAA and CVAAS. *Error bars* denote the standard deviation of replicate analysis

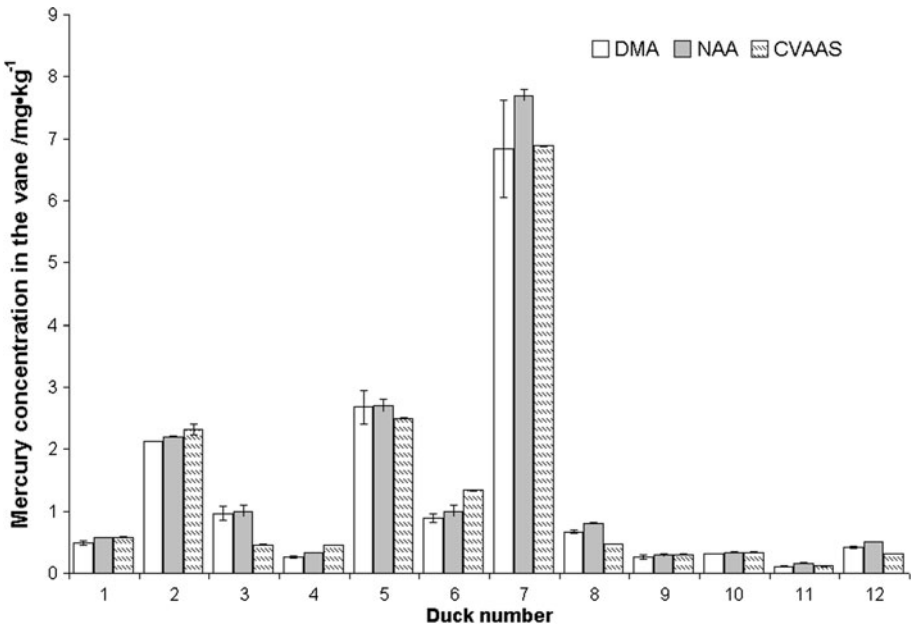

Fig. 2 Comparison of vane-mercury concentrations for DMA, NAA and CVAAS. *Error bars* denote the standard deviation of replicate analysis

and ease of operation [40]. Nevertheless, DMA is an attractive alternative as it is also easy to use and eliminates the requirement for sample pretreatment. Samples analyzed via DMA were performed in duplicate, while CVAAS samples were looked at in triplicate.

The results from both the CVAAS and DMA analyses compare favourably with the INAA results, with DMA performing slightly better. Rachis and vane results are shown in Figs. 1 and 2, respectively. With only one exception, mercury concentrations in the vane, when measured with INAA and DMA, were within 30% of each other. However, when comparing INAA to CVAAS, values were consistent (within 30%) only half of the time; CVAAS appeared to under-report mercury concentrations in the feather vanes. Rachis concentrations, as measured by INAA and DMA, were also all within 30% of each other. Again, CVAAS values were within INAA values only half of the time and like in the vane analysis, CVAAS appears to under-report concentrations. The discrepancy in the CVAAS values is perhaps a function of the requirement for sample digestion; errors can arise during sample digestion as a result of insufficient oxidation to liberate the analyte from the matrix [41], incomplete conversion of the element into a form that can be easily detected (in this case, the conversion of organomercury into mercury(II)) [42–45] or loss of vapour [46, 47]. Despite the lower CVAAS numbers, the correlation between CVAAS and INAA results was greater than 99.8% for the vane portion and over 70% for the rachis segment. Correlations between INAA and DMA were greater than 99.8% for both feather portions. Given these findings, in conjunction with the results from the certified reference material evaluations, INAA appears to be a suitable method of analysis for the determination of elemental contamination in avian feathers. In fact, the ability to analyze feathers non-destructively for multiple elements using only a single sample makes INAA the preferred method for this matrix.

Conclusions

Mallard feathers were successfully analysed by INAA for antimony, arsenic, chromium, mercury and selenium. Elevated concentrations were found for chromium and mercury, indicating a necessity for further monitoring studies both for the protection of the Mallards and the individuals who consume their tissues; based on feather concentrations alone, at least two of the ducks examined over course of this study could be considered dangerously contaminated [48, 49]. To corroborate the validity of using INAA to assess the chemical composition of feather samples, results were compared against those obtained via CVAAS and DMA. While DMA compared more favourably than CVAAS, both techniques produced results comparable to those obtained via INAA. While INAA has been used previously to examine contaminant levels in European bird feathers, this is, to our knowledge, the first time this technique has been used to look at North American feather samples. Additionally, this is the first time that INAA results for feather samples have been verified by comparison with results from both CVAAS and DMA. Based on the results of this study, INAA should be considered as a suitable choice for trace elemental determinations in feather samples. Future research from this group will focus on using INAA to examine the relationships between contamination levels measured in the feathers and those measured elsewhere in the body.

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