Determination of Total Iodine in Seed and Plant-Derived Feed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

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Abstract

Iodine is an essential trace mineral for the human body because it is necessary in the synthesis of the thyroid hormones triiodothyronine (T3) and thyroxine (T4). Iodine was first added to salt in the United States in 1924 to prevent iodine deficiency. Now it is added to animal feed to improve animal health and increase the iodine content of common foods, such as milk.[1]

Iodine content in feed has been determined by ashing and titration according to AOAC official methods 934.02 and 935.14. Gravimetry and gamma-ray spectroscopy are also the common approaches used in AOAC methods. With the recent adoption of AOAC methods 2012.15 and 2012.14, ICP-MS has begun to take the lead role in trace iodine quantification. Here we present a new method of sample preparation and ICP-MS determination of total iodine.

After microwave assisted base digestion in choline hydroxide solution, solubilization of iodine from seed and plant-derived feed was achieved. Iodine was detected by an ICP-MS with a Collection /Reaction Interface (CRI). This method is fully validated and has a reporting limit of 0.1 µg/g.

Objective

Develop and validate an analytical method for the determination of total iodine in plant-derived animal feed.

Materials and Methods

- **Chemicals and Reagents**
  - Iodine standards were prepared in choline hydroxide solution.
  - Tellurium of 0.02 µg/mL concentration was used as internal standard
- **Test Matrices**
  - The method was validated using Purina Certified Rodent Diet 5002 (feed) and dent corn (*Zea mays*).
- **Equipment**
  - MARS 5 microwave system, MARSXpress vessels, CEM (Matthews, NC, USA)
  - SC-4DX auto-sampler, Elemental Scientific (Omaha, NE, USA)
  - Inductively Coupled Plasma Mass Spectrometer (ICP-MS), Bruker 820-MS and Bruker Quantum™ software, Bruker Daltonics (Fremont, CA, USA)
  - ELGA Purelab Flex water purification system, ELGA (Woodridge, IL, USA)
  - Retsch grinder, Retsch (Haan, Germany)
  - PSF syringe filters, Pall (Port Washington, NY, USA)

Materials and Methods

- **Sample Preparation**
  - Frozen samples were ground to pass through 0.75 mm sieve.
  - 0.25 g sample was weighed.
  - 20 mL of Choline hydroxide and a stir bar was added.
  - Sample dissolution was carried out following the microwave program in Table 1.
  - Digested samples were diluted to 50 mL and filtered through PSF syringe filters.

Table 1. Microwave program.

Power (watts)	Max%	Ramp (min)	Temperature (°C)	S	Hold (min)
1600	100	20	170	3	10-15

Microwave: MARS 5, S = stir.

Materials and Methods

Table 2. ICP-MS parameters (non-CRI).

	Parameters	Settings
Gas flow (L/min)	Plasma Flow	17.5
	Auxiliary Flow	1.8
	Nebulizer Flow	1.00
	Sheath Flow	0.19
CRI Gases (mL/min)	Skimmer (with H2)	OFF
RF	RF Power (kW)	1.5
Sample Introduction	Sampling Depth (mm)	7.0
	Pump Rate (rpm)	6
	Stabilization Time (s)	55
	Spray Chamber (°C)	3
Ion Optics (volts)	First Extraction Lens	-1.00
	Second Extraction Lens	-189
	Third Extraction Lens	-242
	Corner Lens	-179
	Mirror Lens Left	45
	Mirror Lens Right	38
	Mirror Lens Bottom	29
	Entrance Lens	1.00
	Entrance Plate	-41
	Fringe Bias	-2.8
	Pole Bias	0.00
Quadrupole Scan	Scan Mode	Peak Hopping
	Dwell Time (ms)	20
	Points Per Peak	1
	Scans/Replicate	30
	Replicates/Sample	5

Analyte: ^{127}I
Calibration standards: 0.5, 2.5, 10 and 50 ng/mL
Internal standard: ^{125}Te
Calibration Parameters: Linear, Minimum Correlation Coefficient 0.99, Weighted Fit

Results

Seed and Feed

Table 3. Test results of commercial available maize grain seed and rodent diet.

Matrices	Content (µg/g)	Certified Content (µg/g)	RSD (%)	Recovery (%)
Maize Grain	< 0.1	N/A	8.08*	98.5
Rodent Diet	1.00 ± 0.101	1.03 ± 0.96 [2]	10.0	98.8

The calculations were based on seven samples and three spikes.

***Calculated using the spiked samples.**

Results

Certified Reference Material (CRM)

Table 4. EPL Test results of NIST CRM 1573a (tomato leaves), 1547 (peach leaves), and 1849a (Infant/Adult Nutritional Formula).

CRM	Test Value (µg/g)	Certified/Reference Value (µg/g)
1547 Peach Leaves	0.3	0.3*
1573a Tomato Leaves	0.82	0.85*
1849a Infant/Adult Nutritional Formula	1.22	1.29 (± 0.11)

*** Reference values.**

Discussion

Test Results

- The rodent diet was derived from maize grain. RSD and recovery results of maize grain and rodent diet showed good accuracy and precision in total iodine determination (Table 3).
- Our test results of multiple CRMs were within the range of the Certified or Reference Values (Table 4).

Discussion

Sample Preparation

- Tetramethylammonium hydroxide (TMAH) had been successfully used in iodine determination[3] until the recent severe poison cases[4] and toxicity studies[5].
- Choline is an essential vitamin for humans. Choline hydroxide is a strong organic base ($pK_a = 5$)[6]. It was demenstrated to be a successful replacement for TMAH.
- High purity choline hydroxide could improve detection sensitivity and analytical precision should it be commercially available.
- Low leachable metal content containers and base washed (following the EPL SOP) containers were utilized throughout the analysis.
- Test precision could be further improved should samples be ground to a smaller particle size (≤ 300µm).[7]

Discussion

ICP-MS Analysis

Tellurium has similar properties to iodine (Table 5). It was proved to be a sufficient internal standard for iodine analysis in choline solution.

Dilute ammonium hydroxide was used as auto-sampler rinse solution and sample carrier solution to efficiently eliminate carryover.

CRI (collision/reaction interface) gas (hydrogen) might be helpful to remove polyatomic interferences.

Table 5. Comparison of Tellurium and Iodine.

	Atomic Number	Isotopes	Atomic Weight	First Ionization Potential
Te	52	120, 122, 123, 124, 125, 126, 128	127.6	9.01
I	53	127	126.9	10.451

Conclusions

The EPL analytical method was successfully validated with satisfactory accuracy and precision for both seed & feed and CRM samples.

Sensitivity and reporting limit (0.1 µg/g) fits the requirements of European Food Safety Authority[8] and National Research Council in the USA[9-11].

To our knowledge, this is the first publication of using choline hydroxide in iodine analysis.

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