Determination of ^{125}I, ^{129}I and ^{131}I in Milk

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Abstract

The determination of iodine radioisotopes in cow's milk has been reconsidered and improved in order to reach higher accuracy and sensitivity and a shorter analysis time.

Introduction

Our laboratory is involved in the systematic control of radioactivity in food products.

The relevance of radioisotopes of iodine in milk in biological, physical, chemical and geological systems, the increasing diagnostic and therapeutic use of ^{125}I and ^{131}I in nuclear medicine, and the potential release of ^{129}I to the environment connected with nuclear energy activities, gave rise to considerable interest in the radioiodine in cow's milk. The air-grass-cow-milk-man pathway is a major route of radiation exposure of human thyroid.

Assuming an average man intake of 1 l milk day^{-1}, using the International Commission on Radiological Protection [1] values for maximum permissible radioiodine concentration in water, and adopting an additional safety factor of ten, one can estimate the allowable concentration in milk to be 8.0 pCi/l for ^{125}I, 1.6 pCi/l for ^{129}I and 8.0 pCi/l for ^{131}I.

In the present control work the analytical determination method of radioiodine isotopes in milk has been improved as far as reproducibility, sensitivity and time required for analysis are concerned.

Experimental

Reagents and Apparatus

Milk

Fresh samples from typical farming land far away from industrial and urban pollution and from nuclear plant areas were collected.

Inorganic Anion Exchanger: $AgCl–SiO_2$

The preparation was carried out by shaking about 100 g of silica gel (30–70 mesh chromatographic grade) with 200 ml of 0.5 M silver nitrate solution, stirring the solid phase with 300 ml of 0.5 M hydrochloric acid and washing the mixture with water to remove free hydrochloric acid. Then $AgCl–SiO_2$ was dried at 100 °C and stored in the dark to prevent photodecomposition of the silver chloride.

Radioiodine Standard Solutions

The standard solutions of radioisotopes were obtained from the Saclay Centre (^{131}I) and from the Radiochemical Centre, Amersham (^{125}I and ^{129}I).

Reagent-grade chemicals and bidistilled water were used for all solutions.

Potentiometric Measurements

The determination of iodide concentrations was carried out by using an Orion Mod. 94-53 iodide electrode and an Orion mod. 90-01 single junction reference electrode. Potentials were obtained to within ±0.1 mV using an Orion mod. 701A digital millivoltmeter. All potentiometric measurements were carried out in a thermostatted cell (25 ± 0.1 °C) in the dark.

Gamma Counting

The activity measurements of ^{125}I and ^{131}I were carried out by gamma-spectrometry with a 3 in × 3 in NaI(Tl) well-type detector (1.7 cm diameter/5.2 cm depth) coupled to a Northland IT-5400 multichannel analyser.

Beta Counting

The activity measurements of ^{129}I were carried out by liquid scintillation (LSC) double channel, using a Nuclear-Chicago Mod. 4534, which provides a pulse-height output linear with the phototube pulse. The detectors lead was protected by an additional shield to minimize the background count-rate.

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Analytical Determinations

For monitoring purposes, most procedures currently used in milk employ an initial anion exchange concentration step, which is based on the observation that almost all the milk iodine is in the inorganic state as iodide (the remainder being protein-bound) [2] and therefore it is recoverable by ion exchange.

The success of any radiochemical technique based upon the removal of the iodide species is greatly dependent upon the preservation of the milk from the time of sampling to that of analysis. It has been reported that unpreserved milk samples may show significant increases in the protein-bound iodine (PBI) fraction (at 37 °C up to 50% of the iodine can become bound within 2 hr) [3]. The PBI is unavailable for anion exchange, thus its formation greatly decreases the accuracy of the results. By addition of 0.5 M formaldehyde [4] the PBI formation was fully inhibited at any iodide concentrations. In this case the storage time must be known for decay corrections.

Use of a large sample volume (10 l) will invariably result in an increase in sensitivity. However, for the practice of laboratory handling two samples of 5 l each were treated in parallel.

Since it is impossible to measure directly extremely low-level radioiodine in milk, the use of a 5 l sample required a chemical processing of volume reduction to a small residual without loss of radioiodine.

The chemical process involved several steps: pre-concentration with an anion exchanger, purification from matrix, carrier recovery determination, gamma and beta counting.

The stable iodine present previously in all milk samples as iodide was less than 0.2 mg/l; therefore 5 mg/l of iodide as stable iodine carrier was added to 5 l of milk and the chemical recovery was determined. No correction for the initial stable iodine was added, but the approximation thus introduced was less than 4%. In the case of fresh milk obtained from cows bred with iodine-enriched feed, correction of stable iodine should be necessary, so that the determined value of radioiodine recovery will be negatively biased.

When sufficient stable iodide is present in the sample (>2 mg/l) the iodide carrier is not necessary. All radioiodine contained as iodide in 5 l of milk reached immediate equilibrium with the added sodium iodide carrier.

The determinations of iodide concentrations were made by the use of an iodide-specific electrode and a standard addition technique.

The chemical processing for each sample is presented in Fig. 1 [5].

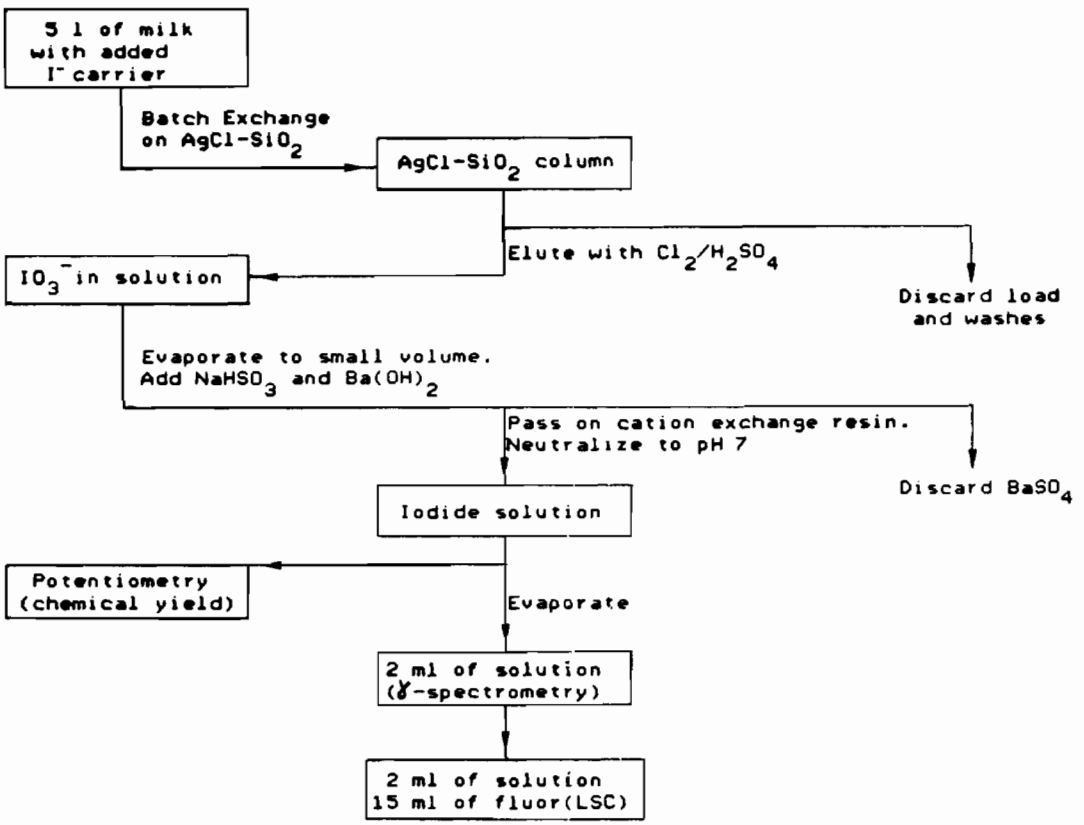

Fig. 1. Outline of the chemical procedure in the determination of radioiodine in milk samples.

(a) Pre-concentration and purification procedure

A milk sample (5 l), after addition of 25 mg of sodium iodide carrier and formaldehyde to 0.5 M concentration, was batch exchanged with 5 g of dry $AgCl–SiO_2$ (three times), where iodide anions are strongly and selectively adsorbed. With the solid phase, after centrifugation for fat elimination, a column was filled from which the iodide was removed as iodate anion by elution with aqueous chlorine solution and sulphuric acid. A further purification was carried out by passing the solution on a cation exchange resin, after having converted again iodine to iodide.

(b) Carrier recovery

The recovered iodide was determined with an ion specific membrane electrode, which is a rapid method for determining the chemical yield, using 2% of the final concentrated solution.

(c) Gamma and beta counting

The type of counting of iodine radionuclides adopted can be rationalized looking at the decay schemes:

^{131}I (half-life: 8 d) decays by several beta-emissions and a gamma-ray of 364.5 KeV.

^{129}I (half-life 1.7×10^7 y) is a low-energy beta-emitter of 150 KeV, decaying to an excited state of ^{129}Xe, from which it is de-excited by the emission of a gamma-ray of 39.6 KeV.

^{125}I (half-life: 60 d) decays 100% by electron capture followed by 35.4 KeV gamma-ray emission. The X-rays (27.4 and 31.0 KeV) emitted after the electron-capture events are in coincidence with the photons emitted in the decay of the 35.4 KeV excited state of ^{125}Te. These photons are either the X-rays following the internal conversion of the 35.4 KeV gamma-ray, or the uncoverted gamma-ray itself. These coincident photons give rise to the characteristic gamma-ray spectrum, which shows a photopeak at 28 KeV due to the single-photon detection of both the X-rays and the 35.4 KeV gamma-rays and a peak at about 60 KeV, due to coincident summing of two X-rays or X-ray and a 35.4 KeV gamma-ray [6, 7].

The measurements of ^{125}I and ^{131}I were carried out by gamma spectrometry with a NaI(Tl) detector (well type), which allows favorable conditions to detect the 60 KeV sum peak of ^{125}I and, of course, the 364.5 KeV gamma-ray of ^{131}I, which were well isolated. The contribution of ^{129}I and ^{131}I to the ^{125}I region was measured and found to be only minor. No interference was shown in the ^{131}I counting.

For beta counting of ^{129}I with a liquid scintillator counter, the channel B was optimized for ^{129}I balance point counting [8], using a standard containing 2 ml of aqueous solution and 15 ml of scintillator (obtained from J. T. Baker Chemical Co. as 'LSC cocktail' for Radioimmunoassay). In order to utilize the Compton distribution of scattered electrons produced in the liquid scintillation solution for quench monitoring [8], using an external solid gamma-ray source of ^{137}Cs, an output of the LSC unit was connected to an Intertechnique 5A 40B multichannel analyser.

2 ml of the final solution, after gamma counting, was submitted to LSC for determination of ^{129}I. Correction was made for the presence of ^{125}I; there is no need for ^{131}I correction if decay is allowed.

Results and Conclusions

The chemical recovery of the iodide carrier determined with an ion specific membrane electrode using 2% of each of the final concentrated solutions gave an average value of 43 ± 2%.

The gamma counting efficiencies, using a 3 in × 3 in NaI(Tl) detector well type, of 2 ml of final solution were 35.2% for ^{131}I at 364 KeV, 21.1% for ^{125}I at 60 KeV. The LSC counting efficiencies for ^{129}I and ^{125}I in the same sample were 50.3% and 30.0% respectively.

With these experimental data it is possible to estimate the lower limit of detection (LLD) of iodine radionuclides.

The 'true' net signal (L_D) level which may be *a priori* expected to lead to detection is defined by eqn. (1) [9]:

$$L_D = 2ks = 2k(s_{gross}^2 + s_b^2)^{1/2} \quad (1)$$

where k: coefficient depending on the preselected confidence level, s: standard deviation of the net signal, s_{gross}^2: variance of gross (directly-observed) counting, s_b^2: variance of background counting. At 95% confidence level and 5% risk level, the value of k is 1.645.

The standard deviation is approximately independent of the signal level when the background counting is large; therefore: $s^2 = s_{gross}^2 + s_b^2 = 2s_b^2$ and L_D can be calculated by eqn. (2):

$$L_D = 4.65s_b \quad (2)$$

L_D may be related to the minimum detectable activity a_D by means of: $L_D = k'a_D$, where k′ represents a calibration factor which, while not being involved directly in the statistics of the detection limit, has a fundamental role in optimizing a given procedure. In this field of research k′ concerns the detection efficiency and the chemical recovery. Therefore the minimum detectable activity (pCi), which is generally reported as LLD, is:

$$a_D = \frac{4{,}65s_b}{ER2.22} = \text{LLD}$$

where E: counting efficiency for the respective radionuclides (cpm/dpm) R: chemical recovery; 1/2.22 conversion factor for dpm to pCi.

When the activities of three iodine radionuclides do not interfere, it is possible to estimate the LLD of ^{125}I, ^{129}I, ^{131}I in the following conditions: (1) sample volume of fresh milk 10 l, (2) iodine recovery 43%, (3) counting efficiency 35.2% for ^{131}I, 21.1% for ^{125}I and 50.3% for ^{129}I, (4) counting time 1000 minutes with the background counting rate of 7.5 cpm for ^{125}I, 19.9 cpm for ^{131}I and 14.4 cpm for ^{129}I. These values of LLD are: 0.4 pCi/l for ^{125}I and ^{131}I; 0.2 pCi/l for ^{129}I.

The technique for radioiodine separation used in radiochemical environmental studies must allow both reliable environmental control and high sensitivity. We have therefore compared the sensitivity of the method, defined as LLD, to the maximum permissible radioiodine levels expressed as 1% of the values recommended by the ICRP (Table I).

TABLE I. Comparison between the Maximum Permissible Concentrations and the Values of LLD for Iodine Nuclides.

Matrix		Milk
Sample volume		10 l
Intake		1 l day
1% ICRP permissible dose	^{125}I, ^{131}I	0.8 pCi/l
	^{129}I	0.16 pCi/l
LLD	^{125}I, ^{131}I	0.4 pCi/l
	^{129}I	0.2 pCi/l

To check the method with real samples of fresh milk, known amounts of three radionuclides, of the order of pCi/l, were added to 5 l of milk and the amounts were estimated by comparison with an identical sample where no radionuclide was added (Table II).

From these data we can derive both the values of average percent recovery $\bar{X}$, and the measure of precision using the relationship for a single set of n measurements with $n \leqslant 20$ [10]:

$$\text{confidence limits} = \bar{X} - ts/n^{1/2}$$

where s is the standard deviation and t is the t-table value at the stated confidence level. At 95% confidence level and for a 'degree of freedom' of 10 the value of t is 2.228 [11].

Therefore we get: 101 ± 9 for ^{131}I, 98 ± 4 for ^{125}I and 95 ± 9 for ^{129}I.

These results allow us to get the precision of the improved method in the ^{125}I, ^{129}I and ^{131}I simultaneous determinations.

The time required for the parallel treatment of the two samples was 1.5–2 days for pre-concentration on radioiodine and 3–4 days for overall determination.

The radioiodine levels in cow's milk of most Italian regions proved to be below the LLD values.

These results indicate that the presence of a nuclear power reactor and the increasing use of radioiodine in nuclear medicine does not cause appreciable radiation contamination of the agricultural products in the surrounding areas.

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TABLE II. Comparison between the Added and the Recovered Quantities of ^{125}I, ^{129}I and ^{131}I in 10 l Milk Samples.

Sample	^{131}I (pCi l^{-1})		^{125}I (pCi l^{-1})		^{129}I (pCi l^{-1})	
	Added	Found	Added	Found	Added	Found
1	5.2	4.6 ± 0.2	5.1	5.2 ± 0.2	3.5	4.0 ± 0.2
2	5.2	4.0 ± 0.2	5.1	5.0 ± 0.2	3.5	3.8 ± 0.2
3	5.2	6.0 ± 0.1	5.1	4.8 ± 0.2	3.5	4.2 ± 0.2
4	10.0	11.5 ± 0.3	5.1	4.5 ± 0.2	3.5	3.2 ± 0.2
5	10.0	9.2 ± 0.3	15.0	13.2 ± 0.3	6.0	5.0 ± 0.3
6	10.1	12.0 ± 0.2	15.0	14.8 ± 0.3	6.0	4.5 ± 0.3
7	15.5	17.3 ± 0.4	15.0	14.5 ± 0.4	6.0	5.2 ± 0.3
8	15.5	14.5 ± 0.4	15.0	15.5 ± 0.4	9.5	8.0 ± 0.4
9	15.5	14.8 ± 0.3	15.0	16.0 ± 0.4	9.5	8.2 ± 0.4
10	20.1	18.5 ± 0.4	30.5	28.8 ± 0.5	9.5	8.5 ± 0.4
11	20.2	22.2 ± 0.3	30.5	32.2 ± 0.5	9.5	10.0 ± 0.4

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