

Extractive electrospray ionization mass spectrometry for sensitive detection of gaseous radioactive iodine-129†

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A rapid method based on extractive electrospray ionization mass spectrometry (EESI-MS) has been developed for quantitative detection of trace radioactive molecular iodine-129 ($^{129}\text{I}_2$) in negative ion detection mode in ambient air. For actual air samples, gaseous $^{129}\text{I}_2$ was completely converted into iodine-129 ions ($^{129}\text{I}^-$) by an excess of Na_2SO_3 solution. By adding excess amounts of $^{127}\text{I}_2$ into the solution, the $^{129}\text{I}^-$ ions formed triiodide ion complexes (i.e. $^{129+127*2}\text{I}_3^-$) which were subjected to tandem mass spectrometry experiments to exclude false positives. Quantification of iodine-129 was achieved by quantitatively measuring the characteristic fragment (i.e., $^{129}\text{I}^-$) of the triiodide ion complexes. The calibration curve showed a good linearity within an relatively wide concentration range of 0.01–1000 ppb ($R^2 = 0.991$), a limit of detection (LOD) of 4.5 ppt and a relative standard deviation (RSD) of 4.0–13.1% ($n = 5$). The spiking recovery of this method was found to be 82.6–110.5%. The method had also been successfully applied to detecting the trace amount of gaseous $^{129}\text{I}_2$ released in a simulated nuclear leakage accident, showing a satisfactory result for the tested gaseous samples. The experimental data demonstrated that EESI-MS was a useful tool for quantitative measurement of radioactive iodine in cases such as nuclear leakage, nuclear explosions and related scenarios.

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Introduction

Iodine-129 (^{129}I) species are one of the most important radioactive pollutants in environmental monitoring due to their high radioactivity and persistence. In nature, traces of ^{129}I species in the atmosphere are mainly produced by cosmic ray-induced spallation of xenon and spontaneous fission of uranium in the geosphere.¹ Their chemical forms are quite complex. Particle associated ^{129}I , the gaseous inorganic ^{129}I fraction (such as I_2 , HI, HOI) and the gaseous organic ^{129}I fraction (CHI_3 , CH_2I_2 , $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$, etc.) are approximately 2–30%, 17–35% and 34–98% of the total of ^{129}I species,² respectively. The concentrations of these species also vary with many parameters, such as location, season and climate.³ In the real-world, a large portion of environmental ^{129}I species are mainly due to human nuclear activities.^{1,4} For example, ^{129}I accounts for roughly 1% of materials produced by ^{235}U fission.⁵ The long half-life, fast global transport in troposphere (within approx. 14 days)⁶ and high affinity to the human body make ^{129}I an extremely persistent and harmful radionuclide.

Once a nuclear leak/explosion takes place, a huge amount of ^{129}I species, which are supposed as molecular iodine-129 ($^{129}\text{I}_2$),⁷ will be released into our living environments and pose a fatal threat to a large population of human beings and the ecosystem in and beyond the local area. Japan's Fukushima nuclear power plant leak accident in 2011 and the Chernobyl accident in 1986 are typical examples of such cases. In this situation, rapid quantification of trace ^{129}I species is of paramount importance.

However, fast quantitative detection of ^{129}I in environmental samples still challenges many currently available techniques due to very low concentrations of those samples. Accelerator mass spectrometry (AMS) is an extremely sensitive tool to detect $^{129}\text{I}/^{127}\text{I}$ ratios (approx. 10^{-14})⁸ by measuring AgI after comprehensive and time-consuming (24–48 h) sample pre-treatments.⁹ Radiochemical neutron activation analysis (RNAA) is less sensitive (LOD 10^{-9} to 10^{-10}) but relatively cheaper than AMS, and thus it has been used more widely for detection of the $^{129}\text{I}/^{127}\text{I}$ ratios.^{10,11} Pre-concentration and post-irradiation purification are needed in this method, which also take a much longer time (about tens of hours)¹² before measurements. Both the above methods present strong memory effects for trace measurement¹ and require very expensive instrumentation.^{13,14} Based on emitting high-energy rays (536 keV (99%), 668.5 keV (96%), and 739.5 keV (82%)), gamma-X spectrometry is accurate and low-cost for the determination of ^{129}I without prior chemical separation.^{15,16} Unfortunately, this method also needs long counting time

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(beyond tens of hours) for one measurement. Recently, new exploratory methods based on inductively coupled plasma mass spectrometry (ICP-MS) have been reported for the determination of ^{129}I using positive ion mode.^{17,18} However, serious interferences from ^{129}Xe (originating from impurities in Ar gas) were found in these experiments. A chemical reaction cell containing O_2 had to be used to remove $^{129}\text{Xe}^+$ (by producing XeO^+), which inevitably complicated the experimental arrangements.

Therefore, novel methods with a simple instrumental setup and convenient, rapid operation are particularly interesting for ultratrace ^{129}I detection. As reported, employing a cheap instrument (e.g., ion trap mass spectrometer), extractive electrospray ionization (EESI)^{19,20} has been used for rapid detection of various analytes at sub-ppb levels in different complex matrices without any sample pre-treatments.^{21–25} The online droplet-droplet extraction occurring between the neutral sample droplets and the charged droplets makes EESI powerful for fast detection of radionuclides such as uranyl species²⁶ and uranium isotopic ratio ($^{235}\text{U}/^{238}\text{U}$),²⁷ allowing the LOD of a few 10^{-3} ng l⁻¹ for uranium by utilizing characteristic fragment detected by EESI-MS³. Therefore, EESI-MS is proposed for high throughput sensitive detection of ^{129}I species in air/water samples.

In this work, trace ^{129}I species were detected using EESI-MS/MS experiments. The triiodide ion was utilized as an important medium for enrichment, excluding false positives and quantitative analysis of gaseous $^{129}\text{I}_2$. Because of extreme insolubility, the ^{129}Xe which is the main interference in ICP-MS analysis could be eliminated by enriching $^{129}\text{I}_2$ in water. This method has been proved as a useful technique for rapid detection radioactive $^{129}\text{I}_2$ with high sensitivity.

Experimental section

Reagent and materials

^{129}I standard reference sample was obtained from China Institute of Atomic Energy (CIAE, Beijing, China) which is an aqueous solution of K^{129}I (massic activity, 257.4 Bq g⁻¹; relative expanded uncertainty ($k = 2$), 3.2%; precisely known concentration, 39.40 ppm) and K^{127}I (with much higher but imprecise concentration than K^{129}I) in a quartz ampoule (volume, 5 ml). Calibration samples were prepared by diluting the standard solution with various amounts of deionized water (18 M Ω cm) (provided by the Chemistry Department facility at East China Institute of Technology). Methanol (HPLC grade, Fisher Scientific, Pittsburgh, US) was used as the electrospraying solvent. $^{127}\text{I}_2$ powder (AR., Mingfeng Chemical Reagent Co., Ltd, Wuxi, China) was used to prepare triiodide ions. β -Cyclodextrin (AR., Guangfu Chemical Reagent Co., Ltd. Tianjing, China) was used for entrapping the residual triiodide ions. H_2O_2 (GR., Aladdin Chemistry Co. Ltd, Shanghai, China) and Na_2SO_3 (AR., Sinoparm Chemical Reagent Co. Ltd, Shanghai, China) were used for oxidizing/restoring iodine species. Nitric acid and hydrochloric acid were received from Yantai Shuangshuang Chemical Reagent Co., Ltd (Yantai, China).

Experimental set-up

Like previously reported uranyl species analytical experiments,^{26,27} the key part of experimental setup is schematically shown in Fig. 1, which has been optimized for sensitive analysis of triiodide ions.

Briefly, pure methanol was electrosprayed in the EESI source as extractive solvent with a flow rate of 5 $\mu\text{L min}^{-1}$. Solution samples containing triiodide ions were introduced at the same flow rate as the electrospray solvent (i.e. 5 $\mu\text{L min}^{-1}$) by a gentle stream of pure N_2 (1 MPa). The optimized working voltage of -4.0 kV (described in the following section 'Parameter optimization') was adopted for the negative ion mode. The angle α between the sample plume outlet and the electrospray beam was 60° , which was closely positioned allowing a distance (a , 1.0 mm) between each other. The angle β between the sample outlet and the heated capillary of the Linear Trap Quadrupole (LTQ) Mass Spectrometer instrument (LTQ-XL, San Jose, CA, USA) was 150° . The heated capillary of the LTQ-MS was maintained at an optimal temperature of 150°C (described in the section 'Parameter optimization'). The distance b between the inlet of the LTQ instrument and the electrospray gas outlet was 8.0 mm. The default values of other parameters, advised by the instrument manufacturer, were directly used without optimization. This configuration provided a much better efficiency and sensitivity for the extractive ionization of triiodide ions from the sample solution by EESI. The triiodide ions analysis was performed for model building and real sample analysis under those optimal parameters.

For radioactive sample analysis, the homemade EESI source was sealed to the LTQ mass spectrometer (seen in Fig. 1) for safety reasons, and the compartment was coupled with a ventilation hood. The left-over radioactive triiodide ions were absorbed by β -cyclodextrin-containing aqueous solutions before the exhaust gas entered the ventilation system, ensuring that no radiant matter could be released into the ambient air during the whole analysis.

Safety remarks

Because radioactive samples were involved in this experiment, there was a safety issue concerned with our study. The handling of radioactive samples required special permission. It was very important to make sure that no radionuclides were

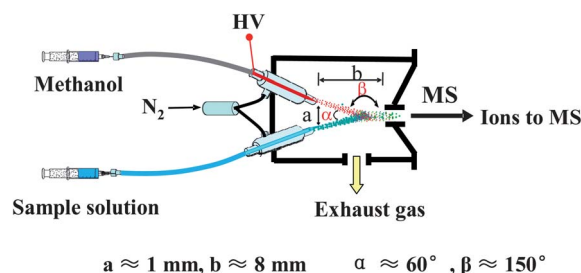


Fig. 1 Schematic diagram of the EESI source equipped with the LTQ-MS for sensitive detection of $^{129}\text{I}_2$. Note that the diagram is not proportionally scaled.

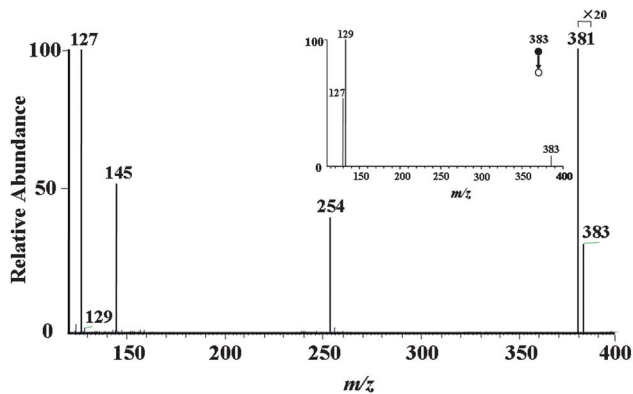


Fig. 2 The normalized chemical fingerprints of triiodide ion ($^{129+127*2}\text{I}_3^-$, 10 ppb) recorded by EESI-MS using the optimized working parameters. A very low signal was recorded at m/z 129 indicated that most of the $^{129}\text{I}^-$ ions were successfully converted to the $^{129+127*2}\text{I}_3^-$. The $^{127*3}\text{I}_3^-$ and $^{129+127*2}\text{I}_3^-$ ions were detected at m/z 381 and m/z 383, respectively. The inset shows the normalized MS^2 spectrum of $^{129+127*2}\text{I}_3^-$ (CID, 30% collision energy, 70 ms).

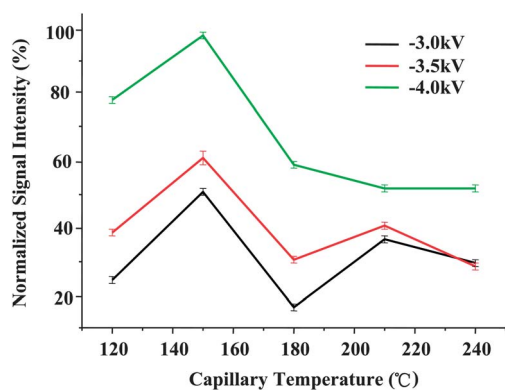


Fig. 3 Optimization of the temperature of capillary and the working voltage of EESI. The concentration of triiodide ion (*i.e.* $^{129+127*2}\text{I}_3^-$) was 10 ppb. Note that the signal intensities at m/z 129 were normalized to 100%, the highest signal available. Each data point represented an average of 6 measurements.

emitted into the laboratory atmosphere. When the solution was diluted and measured, eye protection, gloves, gas mask and protective clothing were used in order to avoid undesirable exposure of skin or inhalation of radiation solvents. All the operation steps were carried out in a chemical hood.

Results and discussion

EESI-MS and MS^2 spectrum of triiodide ions

In this experiment, triiodide ions were simply prepared by using a series of diluted $^{129}\text{I}^-$ standard reference samples (from ppt to ppb level) and excessive amounts of $^{127}\text{I}_2$ for excluding false positives and model building. One prepared triiodide ion of interest consists of one ^{129}I atom and two ^{127}I atoms.

When the target solutions of triiodide ions were directly infused to the EESI source, the chemical fingerprints could be recorded as usual. One normalized (min–max normalization)²⁸ EESI-MS mass spectrum is shown in Fig. 2 in the range between 110 and 400 Da. It is noticeable that the chemical fingerprints of two kind of triiodide ions, *i.e.* $^{127*3}\text{I}_3^-$ and $^{129+127*2}\text{I}_3^-$, were detected with higher sensitivity at m/z 381 and m/z 383. The other three main peaks at m/z 127, 145 and 254 corresponded to $^{127}\text{I}^-$, $[\text{}^{127}\text{I} + \text{H}_2\text{O}]^-$ (loss of 18 mass units in CID spectrum, shown in Fig. S1 in ESI[†]) and $^{127}\text{I}_2^-$ (loss of 127 mass units in CID spectrum, shown in Fig. S2 in ESI[†]), respectively, which were derived from the chemical reactions between dissolved $^{127}\text{I}_2$ and H_2O , because excess $^{127}\text{I}_2$ was added in the prepared calibration samples. Most notably, almost no signal was recorded at m/z 129 indicated that most of the $^{129}\text{I}^-$ ions were successfully absorbed and converted to $^{129+127*2}\text{I}_3^-$, which would be beneficial to the trace analysis.

The peak at m/z 383 was subjected to the tandem MS experiments using mild CID conditions (30% collision energy, 70 ms) and successfully excluded the false positive of triiodide ions. As shown in the inset of Fig. 2, the characteristic fragment ions at m/z 129 exhibited the maximum relative intensity which obviously corresponded to $^{129}\text{I}^-$ of standard samples. The peak at m/z 127 had the second highest signal intensity, which was from the added $^{127}\text{I}_2$. The precursor ions at m/z 383 were almost completely dissociated, which was also beneficial for quantitative analysis under this CID condition.

Typically, the triiodide ion is linear (or nearly linear),²⁹ and the bond energy of I_2-I^- ($13.8 \pm 5.8 \text{ kJ mol}^{-1}$)³⁰ is much lower than that of $\text{I}-\text{I}$ ($152.25 \pm 0.57 \text{ kJ mol}^{-1}$).³⁰ For CID, $\text{I}_3^- \rightarrow \text{I}^- + \text{I}_2$ is the main reaction and the iodine atom has a higher electron affinity (EA) than that of I_2 (3.059 eV vs. $2.46 \pm 0.16 \text{ eV}$).³¹ The dissociation energy of I_3^- is $1.31 \pm 0.06 \text{ eV}$.³¹ Based on this information, it is very clear that the chemical bond between $^{129}\text{I}^-$ and $^{127}\text{I}_2$ of $^{129+127*2}\text{I}_3^-$ is much easier to be broken under the CID conditions, which corresponded well to the

Table 1 Signal responses of $^{129}\text{I}^-$ obtained from the precursor ions of m/z 383

Concentration of triiodide ion/(ppb)	Intensity of $^{129}\text{I}^-$ detected from m/z 383					Mean value	Standard deviation	RSD (%)
0.01	0.012	0.011	0.013	0.014	0.013	0.013	0.001	7.7
0.1	0.031	0.028	0.029	0.036	0.030	0.031	0.003	9.7
1	0.050	0.058	0.065	0.072	0.060	0.061	0.008	13.1
10	0.121	0.130	0.151	0.148	0.152	0.140	0.014	10.0
50	0.381	0.410	0.370	0.412	0.410	0.397	0.020	5.0
100	0.562	0.691	0.724	0.732	0.724	0.687	0.071	10.3
500	2.52	2.70	2.61	2.79	3.23	2.77	0.28	10.1
1000	6.47	6.72	6.80	6.98	7.20	6.83	0.27	4.0

Table 2 Recovery results of ^{129}I species analysis using EESI-MS²

Sample code	MS ² signal intensity ^a (m/z 129)	Content measured ^a (ppb)	Values added (ppb)	Total content measured ^a (ppb)	Values found ^a (ppb)	RSD ^b	Recovery ^c (%)
01	0.320	48.1	50	98.71	50.61	5.5%	101.22%
02	0.650	99.7	400	429.98	330.28	10.1%	82.57%
03	2.81	480.8	500	1033.36	552.56	3.6%	110.51%

^a Mean values of three measurements. ^b RSD for three measurements. ^c Recovery was calculated using the formula: recovery = (values found/values added) \times 100%.

experimental data because the recorded peak intensity at m/z 129 was much higher than that of m/z 127 in the CID spectrum (in the inset of Fig. 2).

Finally, the characteristic fragment ion at m/z 129 (*i.e.* $^{129}\text{I}^-$) in the CID data, which was interference-free from the background spectra (especially for $^{127}\text{I}^-$), was adopted for quantitative analysis.

Parameter optimization

For trace quantitative analysis, it has been demonstrated that the temperature of the heated capillary^{32–34} of the LTQ and working voltages^{33,34} of ESI are among the most important parameters for analytical sensitivity. Therefore, these parameters were investigated in detail. The temperature of capillary was set at five values (*i.e.* 120 °C, 150 °C, 180 °C, 210 °C and 240 °C) in the frequently used temperature range and the working voltage of ESI was adjusted to three specific values (*i.e.* -3.0 kV, -3.5 kV and -4.0 kV) for each temperature condition.

The normalized (min–max normalization) signal intensity at m/z 129 (*i.e.* the characteristic fragment of triiodide ions, 10 ppb) with various temperatures of capillary and working voltages of ESI is shown in Fig. 3. Each data point was measured six times, and the standard deviations (SD) were used to represent the measurement uncertainties. As seen, stable signals (*i.e.* low SD, from 2.9% to 4.7%) could be obtained while the recorded signal intensity varied significantly according to a wide range of temperatures (*i.e.*, 120–240 °C) and working voltages (*i.e.*, -3.0 to -4.0 kV). Under all temperature conditions, the maximum signal intensity was always achieved at the working voltage of -4.0 kV, which was nearly twice the peak intensities of others. On the other hand, the maximum signal intensity was achieved at 150 °C with various working voltages. Therefore, the working voltage of -4 kV and the temperature of 150 °C were employed for the further studies to achieve a reasonable sensitivity and a better stability of signal.

Quantitative calibration of simulated sample analysis

The interference-free characteristic fragment, *i.e.* m/z 129, recorded in the MS² spectrum of m/z 383, was selected for quantitative calibration of iodine-129 species. All the data (*i.e.* the concentration of calibration sample, the peak intensity of m/z 129, and other related statistical values) are summarized in Table 1. Based on those data, a linear correlation between the mass peak intensities at m/z 129 of $^{129+127*2}\text{I}_3^-$ and their concentrations was

obtained within a wide dynamic response range of 0.01–1000 ppb, giving rise to a regression equation of $I_{129} = 0.00658C_{129} + 0.000466$ ($R^2 = 0.991$). The limit of detection (LOD), defined as three times the standard deviation of the blank, was derived to be 4.5 ppt along with an RSD value of 4.0–13.1% ($n = 5$). The low LOD and RSD value indicated that the EESI-MS/MS had good reproducibility and high sensitivity, which was comparable to the result of reported ICP-MS¹⁷ method. The time of sample analysis was much shorter, about 1.0 min per sample (sample loading 0.5 min, data acquisition 0.5 min). The spiking recovery of this method was also investigated. As summarized in Table 2, the recovery ranged 82.57% to 110.51%.

For testing the analytical ability of this method for rapid analysis of real samples after nuclear accidents (*i.e.* gaseous I_2 in air), a simulated experiment was performed. (1) 10 ml $^{129}\text{I}^-$ solution (900 ppb) was firstly put into a 25 ml screw-capped glass phial. (2) After excessive amounts of acidified H_2O_2 (acidified to pH = 2.0 with HCl) were added to the above solution, high purity N_2 gas (450 ml min^{-1}) was immediately introduced into this chemical reactor to blow out the newly synthesised gaseous $^{129}\text{I}_2$ (treated as the real radioactive air pollution after nuclear accident) into excess Na_2SO_3 solution (10 ml, 0.5 ppm) to convert $^{129}\text{I}_2$ to $^{129}\text{I}^-$. (3) Finally, the $^{129}\text{I}^-$ was transferred to triiodide ions by using excess $^{127}\text{I}_2$ for analysis. The result obtained based the above regression equation was 815.42 ppb.

As known, iodine is present in water mostly as IO_3^- and I^- (ref. 9 and 35) which can be easily unified into I^- .^{9,35} This indicates that our method is also practical to detection the low concentration of ^{129}I species in liquids. For example, a detection result of multi-collector ICP-MS showed that ^{129}I sample of some Nevada Test Site (NTS) near-field groundwater samples had reached to a dozen of ppt level.³⁶ In this case, our method can be used directly for rapid analysis.

As seen in the sample preparation progress even for practical samples, the ^{129}Xe and other interferences (such as N_2 , O_2 , CO , CO_2 , NO , SO_2 , CH_4 and some noble gases) in the atmosphere can be effectively eliminated due to their insolubility, or significant differences in molecular weights of new chemical products in water solution. Hence, the prepared analytes have much a simpler matrix and composition for mass analysis. Especially, in case of nuclear emergency, a higher concentration of $^{129}\text{I}_2$ will lead to a much shorter time for enrichment. Therefore, our method provides a potential scheme for quick and convenient detection of $^{129}\text{I}_2$ during the emergency of nuclear accident.

Conclusion

In this paper, the EESI-MS/MS method has been developed and demonstrated to be a rapid and sensitive approach for quantification of trace amounts of ^{129}I species with much less sample pre-treatment compared to the tradition methods such as AMS and NAA. This method provided a successful example for rapid characterization of gaseous $^{129}\text{I}_2$ in atmosphere that also can be used to detect $^{129}\text{I}^-$ ions in water. Our method offers a rapid, sensitive and specific approach for the detection of ^{129}I species, providing potential applications in many fields including nuclear leakage and nuclear explosions. Those findings confirmed that EESI-MS can be employed for the quantitative analysis of inorganic radioactive compounds.

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