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In order to improve the performance of commercially available charcoal filter paper (Toyo Roshi type CP-20, 5 cm diameter, 0.2 cm thick, 50 w/o charcoal content) and charcoal cartridge (Toyo Roshi type CHC-30, 5 cm diameter, 2 cm thick, 30 mesh) for collecting airborne radioiodine released from chemical plants under conditions of high relative humidity and long sampling period, the charcoals were impregnated with triethylendiamine (TEDA), tin iodide (SnI_2), potassium iodide ($KI+I_2$) or potassium rhodanide (KSCN).

The collecting performance of the impregnated charcoals was examined for the airborne iodine released from the radioisotope production plant and the fuel reprocessing plant as a function of sampling period and face velocity by taking the unimpregnated charcoals as a reference.

The charcoals impregnated with TEDA or SnI_2 is greatly improved in the collecting performance as compared with the unimpregnated charcoals and the collection efficiencies of the impregnated charcoal cartridge and of the impregnated charcoal filter paper are maintained at more than 85% and 80% over the period of 14-hr sampling, respectively. It was found, however, that their collecting performance is deteriorated in the presence of chemically reactive gases such as NO_X, DBP. On the other hand, the charcoals impregnated with KI_3 or KSCN are little improved in their collecting performance.

This paper described the results of the performance test in the chemical plants and discuss the effectiveness of the impregnants for collecting of airborne radioiodine.

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化学処理プラントにおける空気モニタリングへの添着活性炭の適用

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放射性沃素捕集の目的で開発した活性炭カートリッジ（CHC−30）および活性炭沪紙（CP−20）の捕集性能，特に高湿度下における長時間サンプリング時の捕集性能を改善するために，活性炭にTEDA，SnI_2，$KI+I_2$あるいはKSCNをそれぞれ添着し，化学処理プラントから排出される沃素を用いて比較実験を行ない，添着活性炭の化学処理プラントの空気モニタリングへの適用性について検討した。

TEDAまたはSnI_2を添着した活性炭においては捕集性能は著しく向上し，14時間サンプリング（相対湿度80％以下）においても，活性炭カートリッジで85％以上活性炭沪紙で80％の捕集効率が得られた。一方$KI+I_2$またはKSCNを添着した場合は，捕集性能の改善はほとんど認められなかった。再処理プラントにおいては，排気系にNOxやDBP等の化学物質が存在するため，添着物質の分解等により，添着効果が減殺されることが分った。

この報告では，沃素製造施設および再処理試験施設で行なった添着活性炭の性能試験の結果を述べるとともに沃素捕集に対する添着物質の有効性について論及する。

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1. Introduction

It has been generally accepted that activated charcoal is most suitable for the purposes of sampling of airborne radioiodine[1] and it has been extensively used as a sampling medium in the field of operational health physics. The collecting performance is, however, deteriorated under atmospheric condition of high relative humidity and also affected considerably by the chemical forms of airborne iodine[2~9]. The monitoring of airborne iodine released from a stack or in working areas during the normal operation as well as the accidental condition is of importance in chemical plants, so that the dependable sampling medium for assessing the concentration of airborne iodine in air is indispensable. In order to improve the collecting performance the activated charcoal was impregnated with various chemical substances[10~12].

To determine the most effective impregnants for the sampling of airborne iodine. The charcoal, which is contained in the commercially available charcoal cartridge (CHC-30) and the charcoal filter paper (CP-20), was impregnated with TEDA, SnI_2, $KI+I_2$ or KSCN which have been found to be effective in collecting airborne iodine in laboratory experiments[12]. These impregnated charcoal cartridge and charcoal filter paper were applied to the sampling of airborne iodine at the Radioisotope Production Plant (RPP) and the Fuel Reprocessing Test Plant (FRTP).

The present paper describes the results on the collecting performance of the impregnated charcoal for airborne iodine generated in the course of chemical processing at both the plants and discusses the effectiveness of the impregnation under the sampling conditions at the chemical plants.

2. Specifications of impregnated charcoal cartridge and charcoal filter paper

The charcoals were impregnated with various kinds of chemical substances in order to examine the effectiveness of the impregnants for collecting airborne iodine. The specifications of the impregnated charcoal cartridges are shown in Table 1.

The impregnated charcoals to be contained in cartridge were provided by the following method: The charcoals (HC-30) were mixed with the alkoholic solution saturated with TEDA or the distillated water solution saturated with one of SnI_2, $KI_3(KI+I_2)$ and KSCN, respectively. The percentage of each impregnant in the charcoals is 10 wt/o, except for SnI_2 whose percentage is 1 wt/o.

The charcoal filter paper (type CP-20[9]) was impregnated with TEDA on the basis of the experimental results obtained for the impregnated charcoal cartridge in addition to ease of impregnation. The percentage of the impregnant in the charcoal was 10 wt/o.

3. Sampling apparatus

In order to compare the collecting performance of the impregnated charcoal and of the unimpregnated charcoal, two same sampling apparatus (one contains the impregnated charcoal and the other the unimpregnated charcoal) were installed in parallel at the exit of air ventilation system. These were drawn through concurrently by a pump as shown in Fig. 1. Humidity and temperature of the sampling air were continuously measured by thermister type hygrometer before the air reached the sampling apparatus, but no attempts were made to control them. The test column consists of 5 impregnated charcoal cartridges or one impregnated charcoal filter paper and 4 impregnated charcoal cartridges.

The other column consists of 5 unimpregnated charcoal cartridges. To determine accurately the collection efficiency of the impregnated charcoal cartridge and charcoal filter paper under various sampling conditions, 3 unimpregnated charcoal cartridges as back-up column and dehumidifier, which ensure the high iodine collection efficiency of the charcoal cartridges by reducing the relative humidity of the sampling air to less than 10%, were connected to each sampling column in series.

Table 1 Specification of impregnated activated charcoal cartridges

Impregnant	Solvent	Percentage of impregnant (w/o)	Temperature during drying (°C)
TEDA	CH_3OH	10	50
SnI_2	H_2O	1	120
$KI+I_2$	H_2O	10 *	70
KSCN	H_2O	10	120

Drying period : 20 h
Activated charcoal : Tsurumi - coal HC-30 (30 mesh coconut shell charcoal)
Effective volume of cartridge : 50mm ×18mm (loading density ; 0.38 g/cm³)
* KI 4 w/o , I_2 6 w/o

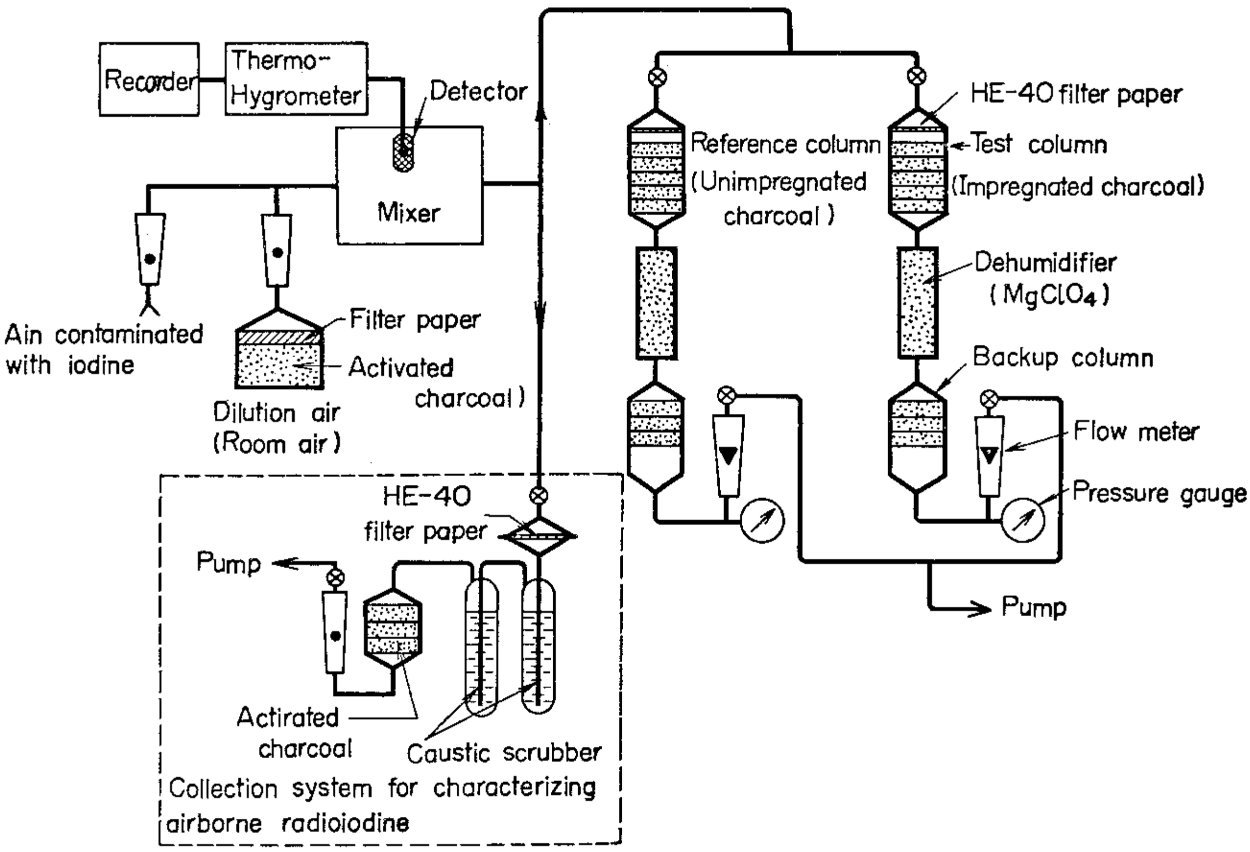

Fig. 1. Diagram of apparatus for testing collection efficiency of activated charcoals

4. Determination of collection efficiency

The collection efficiency of the impregnated charcoals in the test and reference columns was calculated by the following equations, after measuring the ^{131}I activity collected in the test, reference and back-up columns and the dehumidifier.

$$\eta_1(t) = \frac{A_1}{\sum_{i=1}^{5} A_i + \sum_{i=1}^{3} B_i} \times 100\%$$

$$\eta_2(t) = \frac{A_1 + A_2}{\sum_{i=1}^{5} A_i + \sum_{i=1}^{3} B_i} \times 100\%$$

....

$$\eta_5(t) = \frac{\sum_{i=1}^{5} A_i}{\sum_{i=1}^{5} A_i + \sum_{i=1}^{5} B_i} \times 100\%$$

where,

$\eta_1(t)$: collection efficiency of one impregnated (or unimpregnated) charcoal cartridge (18 mm thick) or one impregnated charcoal filter paper at sampling period t.

$\eta_2(t), \cdots, \eta_5(t)$: collection efficiency of two to five impregnated (or unimpregnated) charcoal cartridges at sampling period t, respectively.

A_i : ^{131}I activity collected in each impregnated (or unimpregnated) charcoal cartridge or the impregnated charcoal filter paper in the test (or reference) column (μCi).

B_i : ^{131}I activity collected in each charcoal cartridge in the back-up column (μCi).

The measuring method of ^{131}I collected in the charcoal cartridge and charcoal filter paper was described elsewhere[9)13)]. ^{131}I activity collected in the dehumidifier was measured by 5"ϕ × 4" NaI (Tl) scintilation deteetor with 400 channel PHA after every collection experiment was finished. In all experiments, the ^{131}I activity in the dehumidifier was less than $10^{-3}\%$ of the total activity collected in the columns, so that the activity was not considered in the above equations.

5. Generation of airborne iodine

Airborne iodine generated in each plant during the processing are complicated mixture of various chemical forms of carrier-free iodine and its concentration in air is quite low as compared with one in laboratory test.

5.1 Airborne iodine at the Radioisotope Production Plant

The airborne iodine is generated in a retention tank (capacity 5 m^3) provided for the radioactive waste produced during the ^{131}I processing (distillation method of irradiated telluric acid) and discharged from a stack after passing through the air cleaning system.

The chemical forms of ^{131}I in the liquid waste are analysed by a paper chromatogram[14]: 1 ~ 2% I_2, 4 ~ 13% I^-, 18 ~ 90% IO_3^-, 3 ~ 57% IO_4^-, 2 ~ 17% unidentified.

5.2 Airborne iodine at the Fuel Processing Test Plant

At the FRTP, the airborne iodine-131 is released in the process of the fuel dissolution and discharged from the stack after passing through the air cleaning system composed of NaOH scrubber and high efficiency particulate filter.

The chemical form of airborne iodine after passing through the NaOH scrubber was examined by the radio-gaschromatogram. The results showed that the major part of iodine was HIO_3 and HIO_4, and that only less than 0.5% of the total iodine was organic iodide in which the ratio of CH_3I and C_2H_5I was 4.

5.3 Comparison of properties of airborne iodine

The properties of airborne iodine in each plant was examined by using the air sampling device which is able to characterize the airborne iodine. The sampling device is shown in Fig. 2, which consists of one particulate air filter paper (HE-40), two stages of HaOH scrubber (20 cc, 1N) and a pack of 3 charcoal cartridges. The results obtained by this characterization sampler

are given in Table 2. As seen in Table 2, the major part of airborne iodine generated in the retention tank of the RPP is collected in the charcoal cartridges and only a few percent of airborne iodine is collected in the scrubbers, whereas at the FRTP more than 10% of the airborne iodine is collected in the scrubbers. This indicates that elemental or ionic iodine is present in the discharged air of the FRTP more than in the RPP.
Only less than 0.1% of airborne iodine was collected by the particulate filter paper in both the plants, indicating that the airborne iodine is in the vapor phase and little, if any, iodine is associated with particle.

6. Collecting performance of impregnated charcoal cartridge

The air sampling was carried out at each plant under the following conditions; concentration of airborne iodine $4 \times 10^{-7} \sim 7 \times 10^{-9}$ μCi/cc, relative humidity 60 ~ 80% (24 ~ 28°C), face velocity 8 cm/sec (10 l/min). In this sampling, the impregnated charcoal cartridge was examined for the dependence of collection efficiency on the sampling period. The results obtained are shown in Fig. 2 , in which real lines and dotted lines show the results at the RPP and at the FRTP, respectively. The results at the RPP are summarized as follows: ① The collection efficiency of the unimpregnated charcoal decreases gradually with the increase of sampling period and becomes 95.6% at 12-hr sampling, whereas in the charcoals impregnated with TEDA or SnI_2 it does not decrease appreciably and is maintained at more than 98% even at 14-hr sampling. ② The collection efficiency of the charcoals impregnated with KI_3 or KSCN depends greatly on the sampling period and the collecting performance is not improved by the impregnation. ③ When the sampling air is dried below 10% relative humidity by passing through the $MgClO_4$ column, the unimpregnated charcoals maintain the collection efficiency higher than 97.5%. On the other hand, at the FRTP, although the collecting performance of charcoals was greatly improved by impregnating TEDA or SnI_2 as compared with the unimpregnated charcoals, the impregnated charcoals showed the lower collection efficiencies

Table 2 Performance of iodine characterization sampler*

Samling position at plants	Process during sampling period	Percentage of iodine compound collected on each component of the sampler (%)					
		HE-40 filter paper	NaOH scrubber		Activated charcoal cartridge		
			No.1	No.2	No.1	No.2	No.3
Air exit of liquid waste retention tank at ^{131}I production plant		negligible	1.8	1.2	96.0	0.8	0.2
		small	3.0		97.0		
Exit of exhaust air cleaning system at Fuel Reprocessing Plant	Al - dissolution	negligible	8.3	1.4	86.9	2.6	0.8
		small	9.7		90.3		
	U - dissolution	negligible	16.6	4.9	76.5	1.7	0.3
		small	21.5		78.5		
	After agitation of reacter	negligible	19.4	6.0	66.7	7.3	0.5
		small	25.5		74.5		

Flow rate : 300 cc/min, Sampling period : 3h

*** Samler consists of a HE-40 filter paper and tow caustic scrubbers (1N NaOH 200cc) followed by three activated charcoal cartridges**

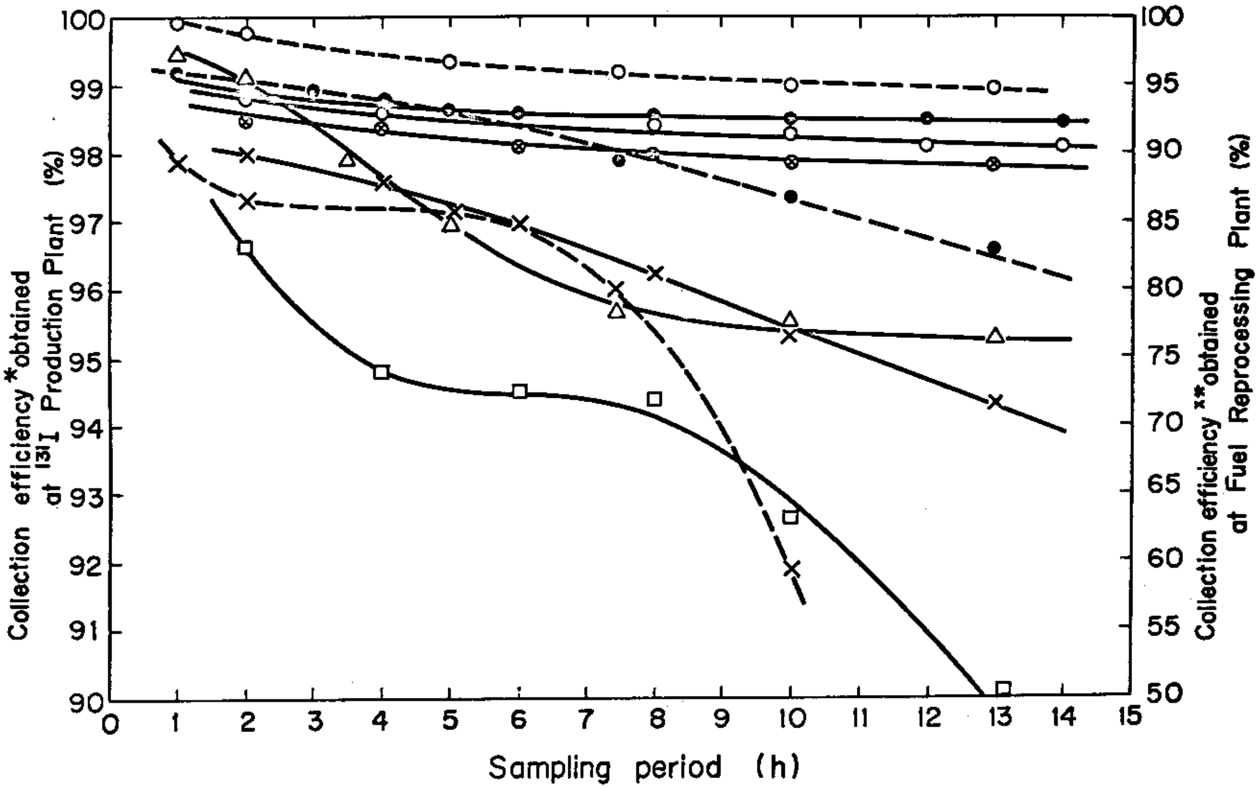

Fig. 2. Efficiency of various impregnated charcoal cartridges for collecting airborne iodine as a function of sampling period

* Solid line : ^{131}I Production Plant
** Dotted line: Fuel Reprocessing Test Plant
● TEDA, O SnI_2, △ $KI+I_2$, □ KSCN,
X unimpregnated (R.H. 60~85%), ⊗ unimpregnated (R.H. < 10%)
Face velocity : 10cm/sec,
^{131}I concentration : 5×10^{-7} μCi/cc
Relative humidity : 60~85% (~24°C)

rather than those obtained at the RPP.

The collection efficiency of the impregnated charcoals was examined as a function of the length of charcoal columns by stacking the cartridges to determine the pertinent length of charcoal cartridge for use of routine air monitoring. The results obtained at the 10-hr sampling are shown in Fig. 3. At both the plants, the collection efficiencies of the charcoals impregnated with TEDA or SnI_2 reach the saturated values at about 4 cm thick, while at the charcoals with the other impregnants much longer charcoal column is needed to reach the maximum collection efficiencies.

7. Collecting performance of impregnated charcoal filter paper

The collecting performance of the charcoal filter paper impregnated with TEDA was examined as a function of the sampling period to apply it to the air monitoring of the chemical plants. The results obtained are shown in Fig. 4. The sampling air was drawn at the face velocity of 8 cm/sec (10 l/min). In the sampling at the RPP, the TEDA impregnated charcoal filter paper is far superior to the unimpregnated one in the collecting performance and its collection efficiency is maintained at more than 95% over the sampling period of 13-hr. On the other hand, in the sampling at the FRTP, the collecting performance is not much improved by the impregnation.

The dependence of collection efficiency on the face velocity was examined by taking the sampling period as a parameter. As shown in Fig. 5, the collection efficiency of the TEDA impregnated charcoal filter paper falls off monotonously with the increase of the face velocity. At the slow face velocity the collection efficiency was found to be much less dependent on the sampling period than at the fast face velocity: The collection efficiency at the face velocity of 8 cm/sec is maintained at more than 95% even at the 12-hr sampling, whereas it falls off to 80% at 40 cm/sec.

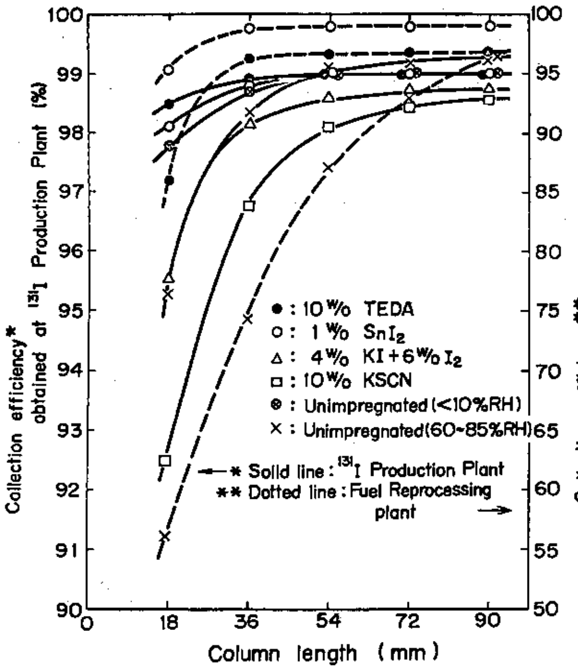

Fig. 3. Effect of length of activated charcoal columns on efficiency for collecting airborne iodine

Sampling period : 10 h
Face velocity : 10cm/sec
^{131}I concentration: $\sim 5 \times 10^{-7}$ μCi/cc
Relative humidity : 60$\sim$85%

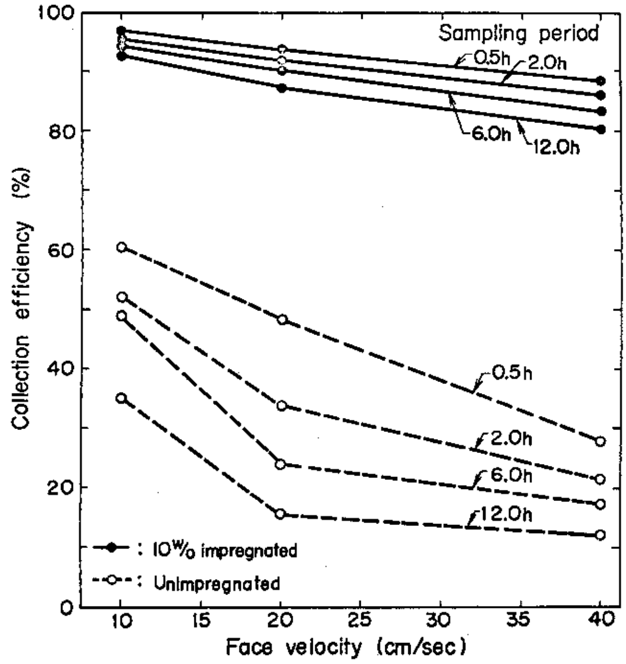

Fig. 5. Effect of face velocity on efficiency of activated charcoal filter paper for collecting airborne iodine

Relative humidity : $\sim$60%

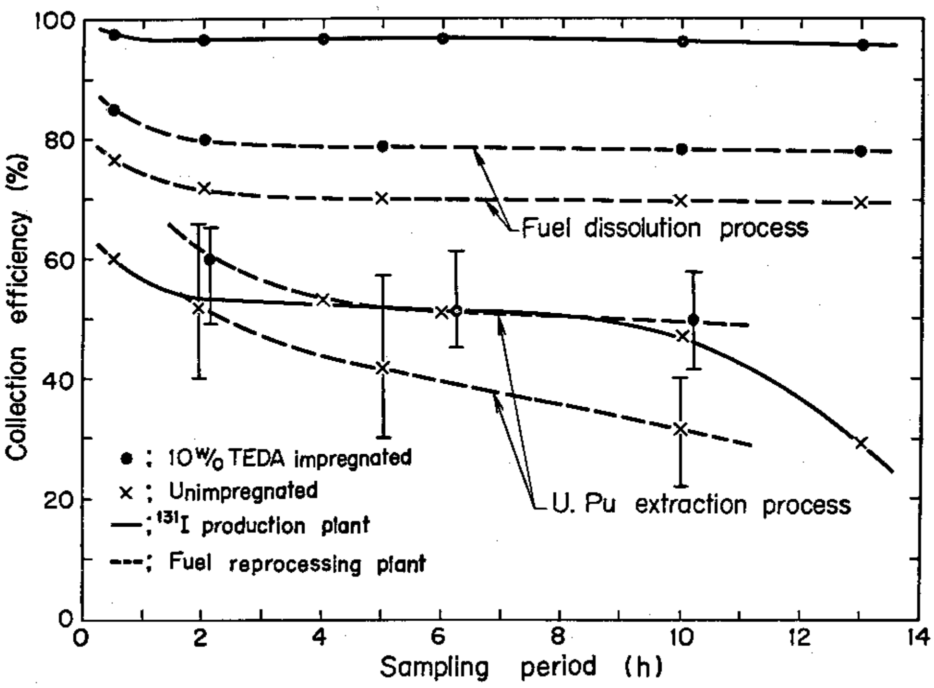

Fig. 4. Effect of TEDA impregnant on efficiency of charcoal filter paper for collecting airborne iodine, which is shown as a function of sampling period

Face velocity : 10 cm/sec
^{131}I concentration : $1 \times 10^{-7} \sim 2 \times 10^{-7}$ μCi/cc
Relative humidity : 60$\sim$85% at the RPP,
$>$80% at the FRTP

8. Discussion

As described in the previous sections, the collecting performance of the charcoals impregnated with TEDA or SnI_2 is much more excellent than the un-impregnated charcoal currently in use under the conditions of high relative humidity. This could be attributed to the facts that TEDA traps the airborne iodine by chemical reaction or isotopic exchange. From the results shown in Table 2, the airborne iodine is expected to be collected more effectively by the charcoals at the FRTP than at the RPP, because the former has a higher proportion of ionic iodide which is collected in the NaOH scrubbers and such iodine species are also collected effectively by the charcoals. Contrary to expectation, however, the charcoal filter paper and charcoal cartridge (both impregnated and unimpregnated) showed the better collecting performance for the airborne iodine at the RPP. This results might be caused by the fact that the off-gas discharged from the FRTP contains a large quantity of chemically active gases or mist such as NO_X, NH_3, NH_4NO_3, which are generated during the fuel dissolution process, and also organic vapor such as dibutyl phosphate and tributyl phosphate. Those chemicals are adsorbed easily in the charcoals, so that the impregnants are decomposed by the chemicals, and/or the chemical reactions between the impregnants and the iodine are prevented, resulting in the reduction of adsorption capacity of the impregnated charcoals.

9. Conclusion

In appling the impregnated charcoals to the air monitoring of chemical plants, the following conclusions are drawn.

(1) Charcoal cartridge impregnated with TEDA or SnI_2 ensures an excellent performance for collecting airborne radioiodine under the conditions of high relative humidity and in the presence of chemically reactive process off-gas.

(2) In using the TEDA impregnated charcoal filter paper, the airborne iodine concentration can be assessed with an error ±10% by taking the collection efficiency as 90% at relative humidity lower than 80% and at sampling period shorter than 12 hr.

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