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Experimental study on iodine chemistry (EXSI) - Containment experiments with methyl iodide

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Abstract

An experimental study on radiolytic decomposition of methyl iodide was conducted in co-operation between VTT and Chalmers University of Technology as a part of the NKS-R programs.
The behaviour of iodine during a severe accident has been studied in several experimental programs, ranging from the large-scale PHEBUS FP tests and intermediate-scale ThAI tests to numerous separate effect studies. In year 2008 the NROI project, a Nordic collaboration studying iodine chemistry in the containment was started. During 2009, oxidation of iodine, especially organic iodine, was studied within the NROI project. The chemistry of organic iodine in the gas phase is still one of the greatest remaining uncertainties concerning iodine behaviour during a severe accident.
During the first year of the NROI project the oxidation of elemental iodine, I2, with ozone and UV-light was investigated. In this study organic iodide, in this case methyl iodide, was investigated in similar conditions as in the NROI-1 project. The experimental facility applied in this study is based on the sampling system built at VTT for the ISTP project CHIP conducted by IRSN. The experimental facility and the measuring technology are sophisticated and unique in the area of nuclear research as well as in the field of aerosol science.
Experimental results showed that the methyl iodide concentration in the facility was reduced with increasing temperature and increasing UVC intensity. Similar behaviour occurred when ozone was present in the system. Formed organic gas species during the decomposition of methyl iodide was mainly formaldehyde and methanol.
Instant and extensive particle formation occurred when methyl iodide was transported through a UVC radiation field and/or when ozone was present. The size of the formed primary particles was about 10 nm and the size of secondary particles was between 50-150 nm. From the SEM-EDX analyses of the particles, the conclusion was drawn that these were some kind of iodine oxides (IxOy). The exact speciation of the formed particles was, however, difficult to obtain because the particles melted and fused together under the electron beam.

Key words

Methyl iodide, nuclear safety, severe accident, containment, ozone

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Summary

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Preface

The gas phase chemistry of methyl iodide has been studied at VTT and Chalmers during year 2010. The performed experiments have increased the knowledge about the behaviour of organic iodide during a severe accident.

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2010-04-29

Christian Ekberg

Contents

1 Introduction

Iodine is one of the fission products released during a severe accident that causes greatest concern, because of its high radiotoxicity in short term and its potential to form several stable volatile gaseous compounds in the containment building [1]. During a severe accident with core meltdown iodine will be transported, mainly as CsI, to the containment where it primarily will enter the aqueous phase in the containment sump (PWR) or the condensation pool (BWR). Through several reaction routes, *e.g.* initiated by radiolysis, iodine will be distributed between the aqueous and the gas phase. The formed gaseous iodine species can be both inorganic and organic. There are several probable routes for formation of organic iodine during a severe accident in the containment. The two major routes are the reactions between elemental iodine and paint surfaces and between iodide and organic radicals in the water phase. The organic iodine species, especially methyl iodide, are even more volatile than I_2.
The behaviour of iodine during a severe accident has been studied in several experimental programs, ranging from the large-scale PHEBUS FP tests and intermediate-scale ThAI tests to smaller studies. Although the understanding of the iodine behaviour has been improved, there still remain several uncertainties. The oxidation behaviour of gaseous iodine in the containment atmosphere is one area in which increased knowledge is sought [2]. In this study the possible formation of iodine oxide aerosols due to radiolytic decomposition of methyl iodide was experimentally investigated. The different formed reaction products, both gaseous and solid, were also analysed. The formation of iodine oxide aerosols has been observed in previous radiolytic oxidation experiments of inorganic iodine [3, 4].

There have been a few experimental studies of the effect of radiolytic decomposition of gaseous organic iodine. Tang *et al.* found that the decomposition was zero-order at concentrations $2.4*10^{-3}$ mol·dm^{-3} and pseudo-first order below $2.4*10^{-7}$ mol·dm^{-3} [5]. The experiments were performed at room temperature. A first-order rate constant was calculated from the data by Dickinson *et al.* to $5.75*10^{-4}$ Gy^{-1} [6]. Tang *et al.* also found that in their experiments I_2 was one of the gaseous products in the radiolytic decomposition of methyl iodide [5].

The reaction between organic iodide and ozone has been investigated by Jimenez *et al*. [7]. The temperature for these experiments was 20 ºC. The amounts of organic iodide (CH_2I_2) and ozone were 5 and 100 ppb, respectively. They found that the particle formation was unnoticeable when the reaction took place in dark conditions. Particle formation required both the presence of ozone and photolysis. Homogenous nucleation was observed in the experiments after inception of photolysis of the gas mixtures under both humid and dry conditions.

Cox *et al.* have performed experiments of CH_3I photolysis with presence of ozone at 303 K [8]. They used low-pressure mercury lamps, UV-quanta emitted mainly at 254 nm, for the photolysis. This can be compared to the UVC radiation used in this study with the main peaks at 185 and 254 nm. Cox *et al.* found that IO radicals were produced by the photolysis of methyl iodide in the presence of ozone through the following reactions:

$$CH_3I + h\nu \rightarrow CH_3 + I \quad (1.1)$$

$$I + O_3 \rightarrow IO + O_2 \quad (1.2)$$

Cox *et al.* also found that I_4O_9 was formed in the system as yellow deposits on the cell surfaces, which were then decomposed to I_2 over extended periods. The speciation of the particles was determined with RAMAN spectroscopy. The authors determined the photo dissociation rate constant for CH_3I to 0.65-1.41*10^{-3} s^{-1}.

2 Experiments

The experimental set-up used for the experiments is shown in Figure 1. The experimental set-up is named the EXSI facility (Facility for EXperimental Study of Iodine chemistry) and was used and built for the previous experiments in the NROI project [3, 4]. The facility has been extensively described elsewhere [3, 4], but some minor changes have been made. The design of the facility is based on the sampling system manufactured previously at VTT [9].

The facility consists of several parts, where the methyl iodide production unit is the first part in line. Gaseous methyl iodide was produced by heating a methyl iodide solution at 30 ºC. The methyl iodide vapour was transported to the UV-furnace by a stream of air. In the first part of the UV-furnace the methyl iodide mixture was diluted with a second stream of air. In some of the experiments this stream consisted of ppm levels of ozone and/or 100% relative humidity. Ozone was produced in an external and adjustable ozone generator. In the experiments with humid atmosphere, air was transported through a 1 L glass flask with about 250 ml of water. The total flow through the system was 6 l/min, but in some of the experiments the flow rate was varied to investigate the reaction kinetics.

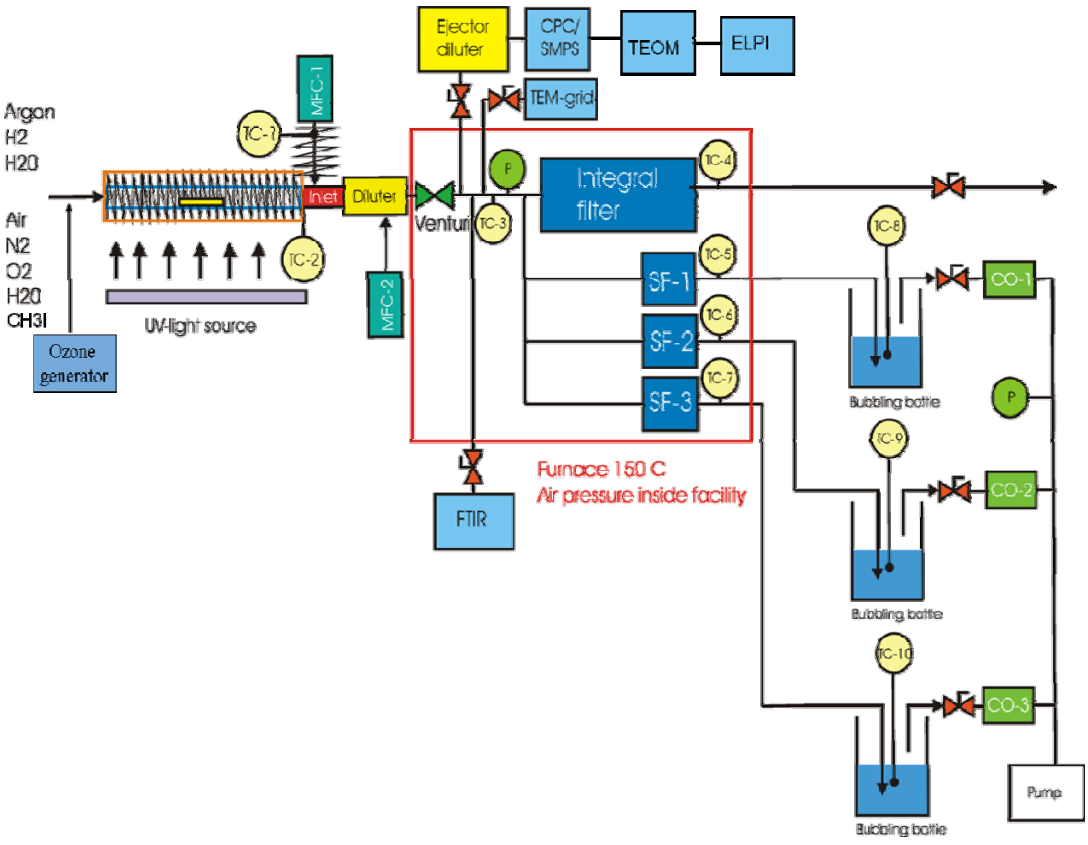

Figure 1: A schematically sketch of the experimental facility used for the experiments.

The gas mixture was then transported through a glass tube of fused silica in the UV-furnace, where it was exposed to UVC-light from four UV-lamps. The radiation spectrum from these lamps had two peaks at 185 nm and 254 nm.

The gas mixture and eventual formed particles were transported to the sampling furnace, where the stream was divided into four lines for analyzes of the mixture. All the tubes in the sampling furnace were made of stainless steel with the inner surfaces covered with a special inert layer called Sulfinert®. The first line was the FTIR-line (Fourier Transform Infra Red), where the methyl iodide and the ozone concentrations were measured as well as the concentration of reaction products like methanol and methyl formiate. Because of this method's inability for detection of homonuclear diatom molecules, any formed elemental iodine (I_2) could not be measured with the FTIR device.
The second line was the aerosol line, which consisted of several analysis instruments for measuring the formed aerosols. These instruments were CPC (Condensation Particle Counter), SMPS (Scanning Mobility Particle Sizer), ELPI (Electrical Low Pressure Impactor) and TEOM (Tapered Element Oscillating. Microbalance). In this line some of the particles were also collected on special copper and carbon grids for speciation analysis with SEM-EDX (Scanning Electron Microscopy – Energy Dispersive X-ray).
The third line in the sampling furnace was the analytical line, which was sub-divided into three separate lines that could be switched open one at a time. Each of these lines consisted of a particle filter and two gas washing bottles in series. This made it possible to have three different conditions during one experiment. The particle filter was made of paper and was used for to collect and determine the amount of solid iodine. After the experiments the paper filters were placed in sodium hydroxide solutions and the iodine content in the solutions was analyzed with ICP-MS (Inductively Coupled Plasma Mass Spectroscopy). The gas washing bottles, containing a solution of 0.02 M sodium thiosulphate and 0.2 M sodium hydroxide, was used to trap the gaseous iodine species, mainly methyl iodide. The iodine content in the gas washing bottles solutions was determined with ICP-MS after the experiments.
The fourth line consisted of a particle filter with the outflow placed in a fume hood. This line was open when the three lines in the analytical line were closed.

In total ten experiments were performed and the experimental matrix can been seen in Table 1. Several different conditions were investigated in order to study the transport of iodine in the system and the particle formation. The parameters that were varied in the experiments were the temperature, the ozone concentration, the UV-radiation intensity, the flow rate, the methyl iodide concentration and the humidity.

Table 1: The experimental matrix.

Experiment	Atmosphere	Temperature (ºC)	V CH_3I (ml)	Total flow (L/min)	O_3 level	UVC
1a	Dry air	120	15	6	7	No
1b	Dry air	120	15	6	10	No
1c	Dry air	120	15	6	0	No
2a	Dry air	120	10	6	0	High
2b	Dry air	120	10	6	1	High
2c	Dry air	120	10	6	1	No
3a	Dry air	120	15	6	0	High
3b	Dry air	120	15	12	0	High
3c	Dry air	120	15	24	0	High
4a	Dry air	120	6	6	0	High
4b	Dry air	120	6	6	0	Low
4c	Dry air	120	6	6	0	No
5a	Dry air	50	30	6	0	High
5b	Dry air	50	30	6	0	Low
5c	Dry air	50	30	6	0	No
6a	Dry air	90	30	6	0	High
6b	Dry air	90	30	6	0	Low
6c	Dry air	90	30	6	0	No
7a	Wet air	120	30	6	10	No
7b	Wet air	120	30	6	0	High
7c	Wet air	120	30	6	0	No
8a	Wet air	120	30	6	0	No
8b	Wet air	120	30	6	0	High
8c	Wet air	120	30	6	1	No
9a	Dry air	90	30	6	0	High
9b	Dry air	90	30	6	0	Low
9c	Dry air	90	30	6	0	No
10a	Dry air	120	30	6	0	High
10b	Dry air	120	30	6	0	Low
10c	Dry air	120	30	6	0	No

3 Results

3.1 General results from the experiments

Preliminary results from the ten experiments can be seen in Table 2. A few complementary experiments will be done in the nearest future. There were some problems with the measuring of the ozone concentration with the FTIR device, due to an unreliable reference. So, in this report the ozone generator levels (0, 1, 5, 7, 10) are shown to allow the reader to follow the trend in the reaction between ozone and methyl iodide. Some ozone measurements will be performed in the future to define the actual concentration of ozone in the system, both at the inlet to the UV-furnace and at the outlet of the sampling furnace.

Table 2: Some results from the main experiments.

Experiment	CH_3I (ppm)	Particle mass (mg/m^3)	iodine as gas (mmol)	iodine as particles (mmol)
1a	2120	280	0.84	8.3E-02
1b	NA	298	0.94	1.5E-01
1c	NA	0	1.02	2.0E-06
2a	3249	21	3.05	1.5E-04
2b	2746	450	1.45	3.7E-02
2c	2294	75	0.64	8.5E-03
3a	3994	7.0	1.21	1.6E-04
3b	2498	4.3	1.60	1.4E-04
3c	2095	2.7	1.22	1.9E-04
4a	3.6	7.7	0.04	2.3E-03
4b	3.5	1.9	0.05	5.3E-04
4c	2.9	0.81	0.03	1.2E-05
5a	5419	3.8	3.27	1.2E-03
5b	5567	0.8	1.74	1.6E-04
5c	5425	0.7	2.20	1.0E-05
6a	2258	4.5	1.16	8.1E-04
6b	2372	0.7	1.48	6.4E-05
6c	2452	0.2	1.27	5.9E-06
7a	2346	1227	1.61	9.7E+01
7b	3751	NA	0.06	5.3E-06
7c	3645	NA	0.31	5.3E-06
8a	3729	NA	1.58	3.9E-05
8b	3475	NA	2.24	4.9E-05
8c	3464	NA	1.61	3.6E-02
9a	3052	7	1.16	8.1E-04
9b	3098	1.3	1.48	6.4E-05
9c	3245	0.4	1.27	5.9E-06
10a	2702	388	1.70	1.3E-04
10b	2763	302	1.89	1.4E-05
10c	2849	69	1.39	7.9E-06

The particle formation was extensive and instant when methyl iodide was transported through the facility simultaneously with ozone. Similar particle production was observed when UVC

radiation was used in the UV-furnace. The behaviour of the particle formation is described further in section 3.4.

3.2 Gaseous reaction products

The methyl iodide concentration was relatively high in the majority of the experiments, compared to severe accident conditions. The changes in methyl iodide concentration, measured by FTIR, were sometimes very small, when *e.g.* the UVC radiation intensity was changed. However, the main trends in the data were possible to discern (Fig. 2). The methyl iodide concentration decreased with increasing intensity of the present UVC radiation. The methyl iodide concentration seems also to vary with the temperature. The higher temperature the lower is the methyl iodide concentration in the facility. The highest methyl iodide concentration was achieved in the experiment (exp. 5) with the lowest temperature, 50 ºC. In this experiment it was not any clear trend in the methyl iodide concentration, increased radiation gives a decreased CH_3I concentration (Fig. 2). The maximum methyl iodide concentration was obtained when at the second highest UVC level, which is difficult to explain. However, this experiment at 50 ºC will be repeated to confirm its reproducibility.
From the experiment with ozone and methyl iodide simultaneously present in system, there is not any clear trend in the methyl iodide concentration at varied ozone production levels. However, in the humid experiment 7 and 8 there was a clear tendency, increased O_3 concentration resulted in a decreased CH_3I concentration. The effect of ozone on the methyl iodide concentration will be investigated further in the nearest future.

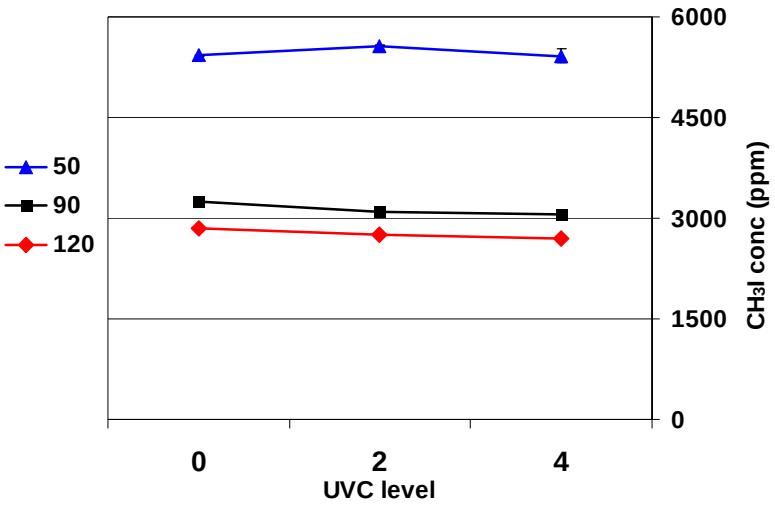

Figure 2: The methyl iodide concentration at different temperatures and different UVC intensity.

The different gas reaction products formed during the experiments were measured with FTIR. These analyses showed that formaldehyde and methanol were the main organic reaction products formed in the decomposition of methyl iodide. Figure 3 is showing a typical FTIR diagram from experiment 10. When the UVC radiation was started after ~1000 s, an immediate production of methanol and formaldehyde began. When the UVC intensity was halved after ~2500 s, the concentration of methanol and formaldehyde decreased with 50 %. After ~4500 s the UVC radiation was turned off and the methanol and formaldehyde

concentrations were below the FTIR detection limit. During this period of the experiment, no or only small amounts (few ppms) of ozone were detectable. Later, at ~6000 s, varying concentrations of ozone produced from the ozone generator were added to the experimental system. The formation of methanol and especially formaldehyde was then even higher compared to the experiments with only UVC radiation (Fig. 3).

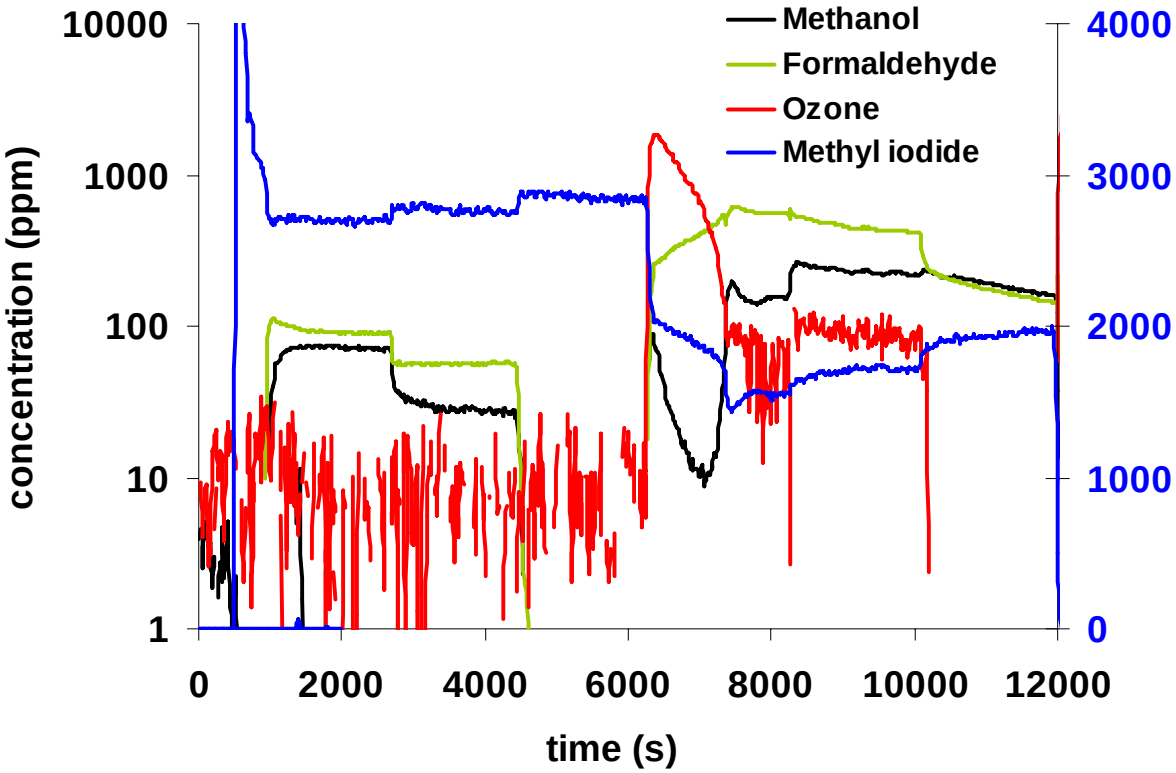

Figure 3. FTIR data of the main gaseous species in the facility during experiment 10. Observe that methyl iodide concentration is connected to the right normal axis. The remainder species are connected to the left logarithmic axis.

It is probable that I_2 also was one of the formed gaseous products in the decomposition of methyl iodide, because it has been detected in radiolytic decomposition experiments before [5]. Some evidence that I_2 was formed in the facility were noticed. From the ICP-MS data, section 3.4, it could be seen that most of the iodine in the system was transported as gaseous iodine. The transparent plastic tubes in the outflow of the facility were coloured purple in the experiments with significant particle formation and methyl iodide decomposition. However, as pointed out earlier the presence of I_2 in the system was not possible to confirm, since the FTIR technique can not detect this species (see section 2).

3.3 Reaction mechanisms

3.3.1 UVC reaction mechanism

The formation of iodine oxides in the experiment with only UVC radiation is a rather complex mechanism with several reactions. Two photolysis reactions are suggested as the initial reactions, the decomposition of O_2 and CH_3I:

$$O_2 + h\nu \rightarrow O + O \quad (3.1)$$

$$CH_3I + h\nu \rightarrow CH_3 + I \quad (3.2)$$

The oxygen and iodine radicals then can react with each other and form I_xO_y particles, via reactions (3.3), (3.4) and (3.5).

$$I + I \rightarrow I_2 \quad (3.3)$$

$$I_2 + O \rightarrow IO + I \quad (3.4)$$

$$IO + IO \rightarrow IO_2 + I \text{ or } I_2O_2 \ldots \rightarrow I_xO_y \quad (3.5)$$

The reaction species detected by the FTIR device, see section 3.2, formaldehyde (HCHO) and methanol (CH_3OH) are formed from the photolysis induced specie CH_3:

$$CH_3 + O_2 \rightarrow CH_3O_2 \quad (3.6)$$

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3O + CH_3O + O_2 \rightarrow CH_3OH + HCHO + O_2 \quad (3.7)$$

3.3.2 Ozone reaction mechanism

The reaction mechanism for the reaction between ozone and methyl iodide, (reaction 3.8), is not fully explained yet. Two possible mechanisms are suggested; either the ozone molecule is decomposed to O_2 and O· that further react with CH_3I, or there is a direct reaction between ozone and methyl iodide [10]. Collaboration has been undertaken with researchers in Great Britain in order to do mechanistic modelling of the experiments in this project, but the work is still under progress [10]. As of today, it seems that more information and experiments are needed for better understanding of the reaction mechanism of O_3 and CH_3I.

$$CH_3I + O_3 \rightarrow CH_3 + IO + O_2 \quad (3.8)$$

3.4 Particle formation behaviour

When methyl iodide was transported through the UVC-radiation field in the UV-furnace, an extensive and instant particle formation was started (Fig. 4, Fig. 5 and Fig. 6). The figures show variation of the particle concentration, particle size and particle mass at different temperatures and UVC radiation intensities.
The size of the particle increased with increasing temperature and UVC intensity. The primary particles in all the experiments were rather small, about 10 nm. But due to agglomeration of particles, the size of secondary particles increased to about 100 nm for the experiment at 120 ºC and at the highest UVC intensity level. However, the particle concentration increased with increased UVC radiation intensity, but decreased with increased

temperature. This observation emphasizes the agglomeration behaviour of the particles especially at higher temperatures. The relatively high particle concentration when UVC radiation is not present in the system, probably depends on production of small amounts of ozone produced inside the ELPI instrument.
In the experiments with UVC radiation present, the mass of the particles increased with increasing UVC intensity and temperature. The temperature dependence seems to be linear., The uncertainties in the particle mass data are large, as can be seen in appendix A (Fig. A1). This depends on the relatively small mass of the formed particles during the experiments with UVC radiation present in the system.
The temperature dependence for the particle production was rather surprising. Baston *et al.* did not see any temperature effects on the radiolytic decomposition of methyl iodide in their experiments [11]. A clear temperature dependence of the mass of formed particles was seen in this project, where an increasing temperature resulted in an increasing particle mass (Fig. 6).

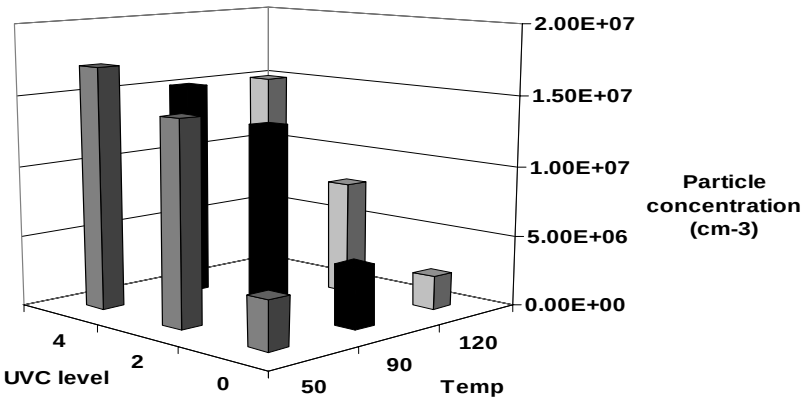

Figure 4. The particle concentration plotted against temperature and the numbers of UVC lamps on.

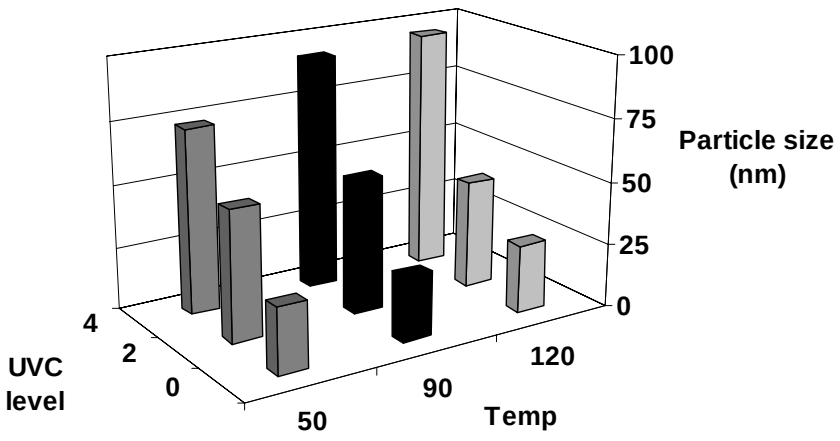

Figure 5. The particle size plotted against the temperature and the UVC level in the system.

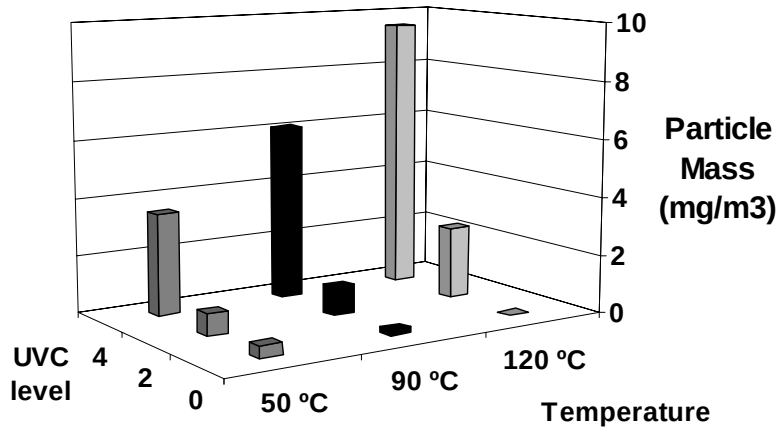

Figure 6. The particle mass plotted against temperature and the numbers of UVC lamps on.

An even more extensive particle formation was observed when ozone, produced from the external ozone generator, was transported simultaneously with methyl iodide through the system. The particle mass, concentration and size were larger compared to the experiment with UVC radiation present (Fig. 7, Fig. A2 and Fig. A3).
At high ozone production levels, the particle mass was about 30 times larger than when maximum UVC radiation was present at the same conditions. The particle mass increased with temperature and ozone concentration, which is similar to the experiments with UVC radiation present. However, complementary experiments will be done to further investigate the differences between UVC radiation and ozone on gaseous methyl iodide chemistry.

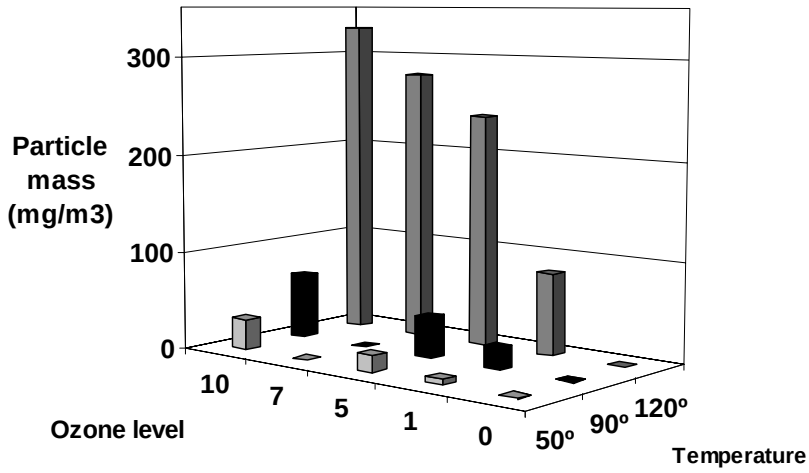

Figure 7. The mass of the formed particles at different ozone levels and temperature

From the experiments with ozone present in the system no clear trends of the variation of the size and concentration of the particles could be seen, in contradiction to the experiments with

only UVC radiation. Neither varied temperature nor ozone concentration influenced the experimental results. The particle size and concentration data can be seen in Fig. A2 in appendix A. The only clear trend is the significantly larger particles at elevated temperatures, 120 ºC, compared to the case at lower temperatures. The size of the largest formed particles in the experiment with ozone present was about 150 nm, and was formed at 120 ºC and at high ozone levels.

The iodine particles and the iodine gas was trapped on paper filters and in gas washing bottles, the procedure is described in section 2. The iodine content on the two trapping units was determined by ICP-MS. The data from the measurements are shown in Figure 8. From these data the conclusion can be made that iodine is transported mainly as gaseous iodine species, *e.g.* CH_3I and I_2. As the FTIR measurement data showed, the CH_3I concentration is just slightly changed when UVC radiation is present in the facility. Although the concentration change is small, similar trends where increasing UVC intensity results in a decreasing CH_3I concentration, are found in the ICP-MS data, supporting the FTIR data. From *e.g.* experiment 9a-9c, there is clear reduction of iodine particles with decreasing UVC intensity.

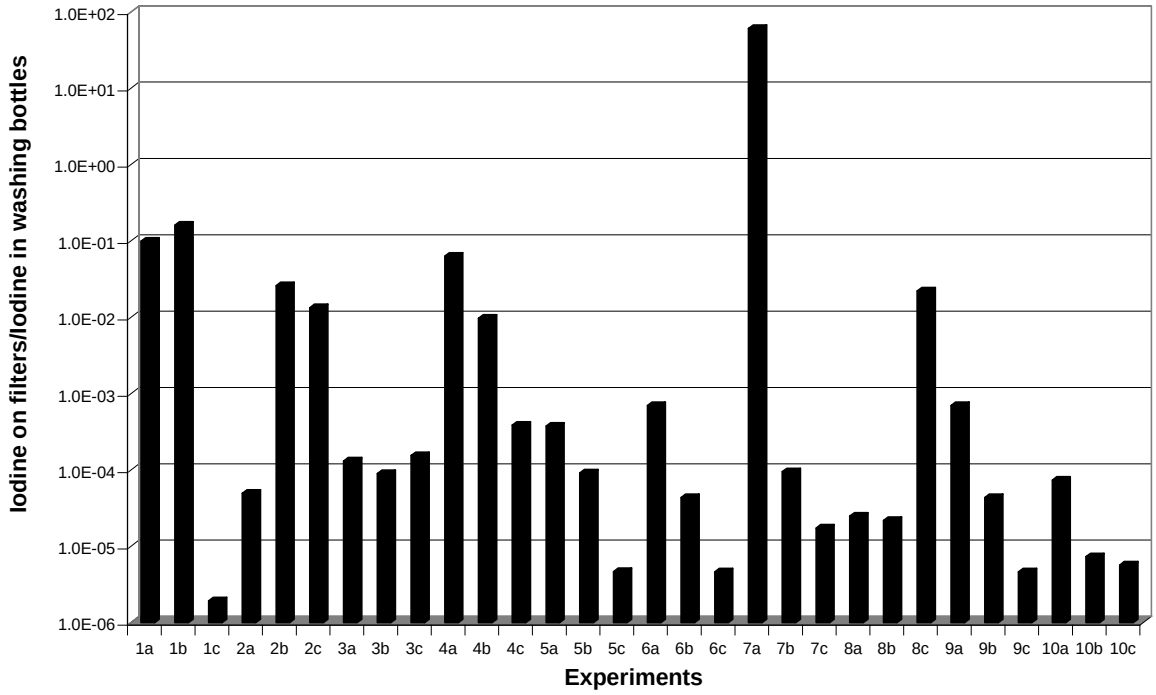

Figure 8. The plot is showing data from the ICP-MS measurements of the iodine trapping units. The plot is showing the ratio between iodine transported through the facility as particles and iodine transported as gas.

The highest proportion of iodine particles in the experiments (1a, 1b, 2b, 2c, 7a and 8c) is observed when ozone is present in the facility. It should be noticed that in the experiments 4a-4c the initial methyl iodide concentration was much lower than in the other experiments. The experiment with the highest proportion of iodine particles is experiment 7a. The conditions in this experiment were high ozone concentration and 100 % relative humidity. In this experiment, apparent marks of red-brown particles on the paper filters were seen (Fig. 9).

Figure 9. Pictures of the filter holders after two experiments. The holder to the left was used at dry conditions, while the holder to the right was used at humid conditions.

3.5 Particle analysis

The trapped particles on the special grids were analyzed with SEM-EDX. The analyses of the particles showed that these contained iodine and oxygen and this was regardless which experiment the particles originated from. The observation strengthens the opinion that aerosols produced from radiation of gaseous iodine are some kind of iodine oxides, of the form I_xO_y. A SEM image of the particles can be seen in Fig. 10. However, the exact speciation is difficult to obtain because the particles were melted, vaporized and fused together under the electron beam during the analyses.
The particles were also trapped on copper grids in some of the experiments. The SEM-EDX analyses of these grids showed that the particles had been decomposed and formed CuI on the surfaces. This indicates that radiolytic composition of methyl iodide in the gas phase can transform gaseous iodine to solid iodide compounds when interaction with different metal surfaces in the containment takes place.

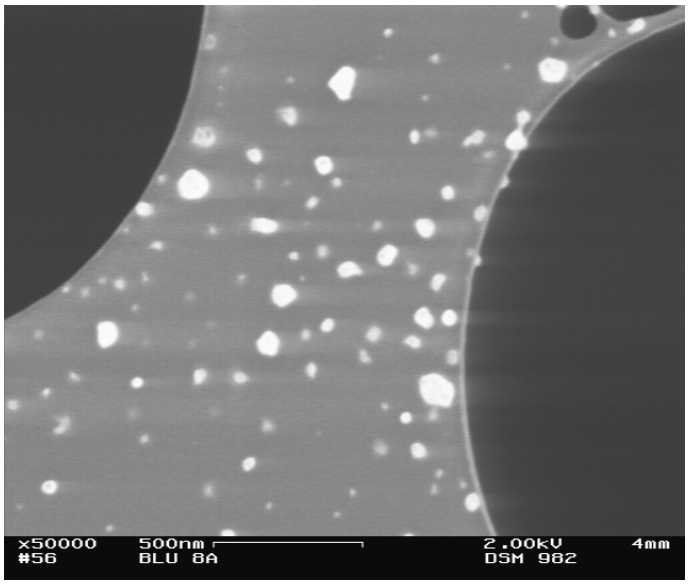

Figure 10: An SEM image of the trapped iodine particles. The white spots are the particles and the light grey area is the carbon grids, where the particles were trapped on.

4 Conclusions

An experimental study on radiolytic decomposition of methyl iodide in containment conditions was carried out at VTT in co-operation with Chalmers University of Technology as a part of the SAFIR2010 and the NKS-R programs. The facility, used for the experiments, built at VTT and the measuring technology is sophisticated and unique in the area of nuclear research as well as in the field of aerosol science.

Some conclusions can be made from the results of the performed experiments:

- The methyl iodide concentration in the facility was reduced with increasing temperature and increasing UVC intensity. Similar behaviour was seen when ozone was present.
- Formed organic gas species during the decomposition of methyl iodide was mainly formaldehyde and methanol.
- Instant and extensive particle formation occurred when methyl iodide was transported through a field of UVC radiation and/or when ozone is present.
- The size of the formed primary particles was about 10 nm and the size of secondary particles was between 50-150 nm.
- From the SEM-EDX analyses of the particles, it is likely that these are some kind of iodine oxides (I_xO_y). But the exact speciation of the formed particles was difficult to obtain, because the particles were melted and fused together under the electron beam.
- The particle mass and particle concentration is higher in humid conditions compared to dry conditions. This is more pronounced at high ozone levels.

5 Acknowledgments

The financial support of the Finnish Research Programme on Nuclear Power Plant Safety (SAFIR), Nordic nuclear safety research (NKS) organisation, Accident Phenomena of Risk Importance (APRI 7) project and the Swedish Centre for Nuclear Technology (SKC) is acknowledged.

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Appendix A

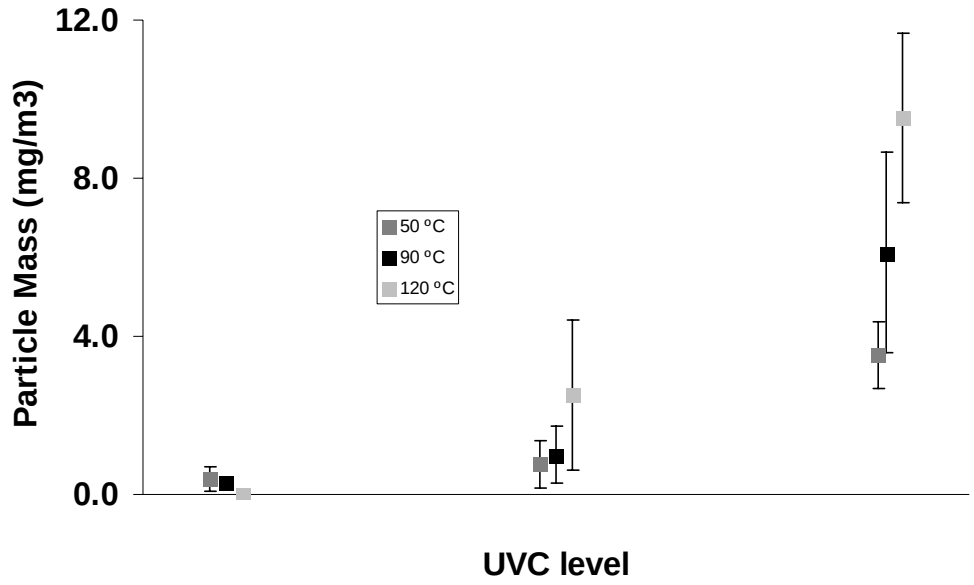

Figure A1: The stand deviation data from the experiments with varying UVC-radiation intensities at different temperatures. Observe that the three groups of data has the same radiation intensities (The group to left without any UVC radiation, the middle group has half maximum of intensity and the group to the right has the maximum radiation intensity).

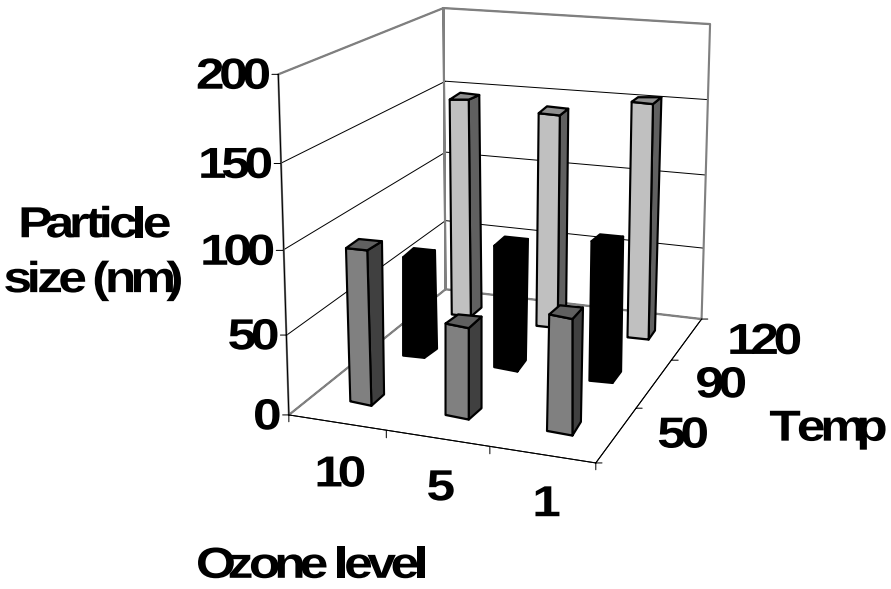

Figure A2. The particle size plotted against the ozone level and the temperature.

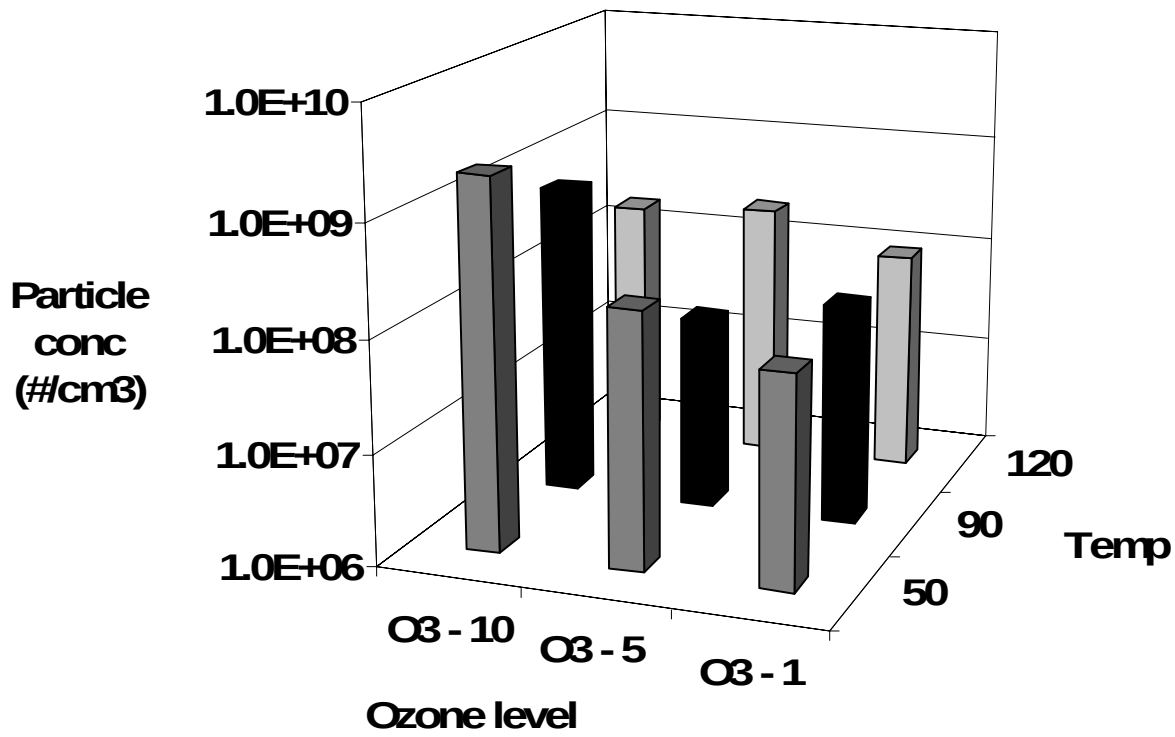

Figure A3. The particle concentration plotted against the temperature and the ozone level production.

Title	Experimental study on iodine chemistry (EXSI) – Containment experiments with methyl iodide
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Abstract

An experimental study on radiolytic decomposition of methyl iodide was conducted in co-operation between VTT and Chalmers University of Technology as a part of the NKS-R programs.

The behaviour of iodine during a severe accident has been studied in several experimental programs, ranging from the large-scale PHEBUS FP tests and intermediate-scale ThAI tests to numerous separate effect studies. In year 2008 the NROI project, a Nordic collaboration studying iodine chemistry in the containment was started. During 2009, oxidation of iodine, especially organic iodine, was studied within the NROI project. The chemistry of organic iodine in the gas phase is still one of the greatest remaining uncertainties concerning iodine behaviour during a severe accident.

During the first year of the NROI project the oxidation of elemental iodine, I2, with ozone and UV-light was investigated. In this study organic iodide, in this case methyl iodide, was investigated in similar conditions as in the NROI-1 project. The experimental facility applied in this study is based on the sampling system built at VTT for the ISTP project CHIP conducted by IRSN. The experimental facility and the measuring technology are sophisticated and unique in the area of nuclear research as well as in the field of aerosol science.

Experimental results showed that the methyl iodide concentration in the facility was reduced with increasing temperature and increasing UVC intensity. Similar behaviour occurred when ozone was present in the system. Formed organic gas species during the decomposition of methyl iodide was mainly formaldehyde and methanol.

Instant and extensive particle formation occurred when methyl iodide was transported through a UVC radiation field and/or when ozone was present. The size of the formed primary particles was about 10 nm and the size of secondary particles was between 50-150 nm. From the SEM-EDX analyses of the particles, the conclusion was drawn that these were some kind of iodine oxides (IxOy). The exact speciation of the formed particles was, however, difficult to obtain because the particles melted and fused together under the electron beam.

Key words Methyl iodide, nuclear safety, severe accident, containment, ozone