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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.
In year 2008 the NROI project, a Nordic collaboration studying iodine chemistry in the containment, was started. During year 2008 (NROI-1) the radiolytic oxidation of elemental iodine was investigated and during 2009 (NROI-2), the radiolytic oxidation of organic iodine was studied. This project (NROI-3) is a continuation of the investigation of the oxidation of organic iodine. The project has been divided into two parts. 1. The aims of the first part were to investigate the effect of ozone and UV-radiation, in dry and humid conditions, on methyl iodide. 2. The second project was about gamma radiation (~20 kGy/h) and methyl iodide in dry and humid conditions.
1. Experimental results showed that the methyl iodide concentration in the facility was reduced with increasing temperature and increasing UV-radiation 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.
The particle formation was instant and extensive when methyl iodide was exposed to ozone and/or radiation at all temperatures. The size of the formed primary particles was about 10 nm and the size of secondary particles was between 50-200 nm. From the SEM-EDX analyses of the particles, the conclusion was drawn that these were some kind of iodine oxides (I_xO_y). However, the correct speciation of the formed particles was difficult to obtain because the particles melted and fused together under the electron beam.
2. The results from this sub-project are more inconsistent and hard to interpret. The particle formation was significant lesser than corresponding experiments when ozone/UV-radiation was used instead of gamma radiation. The transport of gaseous methyl iodide through the facility was much lower than expected for some unknown reason. A “new” reaction product in this kind of experiments was detected, namely iodoform (CHI_3), but the data is rather uncertain.

Key words

severe accidents, iodine, aerosols, methyl iodide, radiolytic oxidation

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Summary

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 year 2008 (NROI-1) the radiolytic oxidation of elemental iodine was investigated and during 2009 (NROI-2), the radiolytic oxidation of organic iodine was studied. This project (NROI-3) is a continuation of the investigation of the oxidation of organic iodine.

The project has been divided into two parts. 1. The aims of the first part were to investigate the effect of ozone and UV-radiation, in dry and humid conditions, on methyl iodide. 2. The second project was about gamma radiation (~20 kGy/h) and methyl iodide in dry and humid conditions.

1. Experimental results showed that the methyl iodide concentration in the facility was reduced with increasing temperature and increasing UV-radiation 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.

The particle formation was instant and extensive when methyl iodide was exposed to ozone and/or radiation at all temperatures. The size of the formed primary particles was about 10 nm and the size of secondary particles was between 50-200 nm. From the SEM-EDX analyses of the particles, the conclusion was drawn that these were some kind of iodine oxides (I_xO_y). However, the correct speciation of the formed particles was difficult to obtain because the particles melted and fused together under the electron beam.

2. The results from this sub-project are more inconsistent and hard to interpret. The particle formation was significant lesser than corresponding experiments when ozone/UV-radiation was used instead of gamma radiation. The transport of gaseous methyl iodide through the facility was much lower than expected for some unknown reason. A "new" reaction product in this kind of experiments was detected, namely iodoform (CHI_3), but the data is rather uncertain.

Confidentiality	Public

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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. Experiments were conducted in May and June 2010 at VTT; the behaviour of methyl iodide exposed to ozone and UV-radiation was studied. In September (2010) experiments were performed at Chalmers; the behaviour of methyl iodide in a strong gamma field was investigated. VTT transported the experimental facility to Chalmers and there it was connected to gamma radiation source.
Experiments were conducted by **Teemu Kärkelä (VTT)** and **Joachim Holm (Chalmers)**. Results of the study are part of their PhD theses.

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2011-04-26

Christian Ekberg

Contents

1 Introduction

Amongst the released fission products iodine causes greatest concern in safety analysis, because its high radiotoxicity in short term and its potential to form several stable very 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 will 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 iodine behaviour has been improved, there still remain a number of points that should be better addressed. The existing knowledge needs to be extended to the interactions of volatile iodine with air radiolysis products in the containment atmosphere, especially to the nature and fate of oxidation products [2]. The formation of iodine oxide aerosols has been observed in previous radiolytic oxidation experiments of both inorganic and organic iodine [3, 4, 5, 6]. In this study the formation of iodine oxide aerosols due to radiolytic decomposition of methyl iodide, exposed to ozone or UV-radiation, was experimentally investigated. The formed reaction products, both gaseous and solid, were also analysed.

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} [7]. 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} [8].

Tang *et al.* [7] proposed a mechanism for the radiolytic destruction of CH_3I, which involved reaction with an activated species:

$$CH_3I + M^* \rightarrow CH_3\cdot + I\cdot + M \quad (1)$$

It is a reasonable assumption that the γ-ray energy is primarily absorbed by air to form active particles, M*, which in turn transfer energy to CH_3I molecules upon collision.

It is generally accepted that the reaction of methyl radicals with oxygen takes place *via* two routes, namely, thermomolecular reaction leading to the formation of methyl peroxide radicals

$$CH_3\cdot + O_2 + M \rightarrow CH_3O_2\cdot + M \quad (2)$$

and bimolecular reaction which gives rise to formaldehyde:

$CH_3\cdot + O_2 \rightarrow HCHO + OH\cdot$ (3)

Formaldehyde, and methanol, has been shown to be formed before in earlier NROI experiment [5, 6].
When the iodine radicals, I·, are recombined, inorganic elemental iodine, I_2, is formed:

$I\cdot + I\cdot + M \rightarrow I_2 + M$ (4)

The last reaction accounts for the formation of I_2 observed in the experiments at high CH_3I concentrations, but would be unlikely to occur at low concentrations where other reactions of I· would be more likely. The reaction between present oxygen and iodine radicals is a possible route for formation of iodine oxides, iodine particles, which has been seen in the previous NROI experiments [3, 4, 5, 6].

The reaction between organic iodide and ozone has been investigated by Jimenez *et al*. [9]. The temperature for these experiments was 20 ºC. The amounts of organic iodide (CH_2I_2 was used as precursor) and ozone were 5 and 100 ppb, respectively. They found that the particle formation was unnoticeable when the reaction took place in dark conditions. The 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 [10]. 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:

$CH_3I + h\nu \rightarrow CH_3 + I$ (5)

$I + O_3 \rightarrow IO + O_2$ (6)

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 $0.65\text{-}1.41*10^{-3}$ s^{-1}.

1.1 Theory

1.1.1 UVC reaction mechanism

The formation of iodine oxides in the experiment with only UV-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:

$O_2 + h\nu \rightarrow O + O$ (7)

$$CH_3I + h\nu \rightarrow CH_3 + I \quad (8)$$

The oxygen and iodine radicals then can react with each other and form I_xO_y particles, via reactions (9), (10) and (11).

$$I + I \rightarrow I_2 \quad (9)$$

$$I_2 + O \rightarrow IO + I \quad (10)$$

$$IO + IO \rightarrow IO_2 + I \text{ or } I_2O_2 \ldots \rightarrow I_xO_y \quad (11)$$

The reaction species formaldehyde (HCHO) and methanol (CH_3OH) are formed from the photolysis induced specie CH_3:

$$CH_3 + O_2 \rightarrow CH_3O_2 \quad (12)$$

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3O + CH_3O + O_2 \rightarrow CH_3OH + HCHO + O_2 \quad (13)$$

1.1.2 Ozone reaction mechanism

The reaction mechanism for the reaction between ozone and methyl iodide, (reaction 14), is not fully understandable yet. Two possible mechanisms are suggested; either the ozone molecule is decomposed to O_2 and $O\cdot$ that further react with CH_3I, or there is a direct reaction between ozone and methyl iodide [11, 12].

$$CH_3I + O_3 \rightarrow CH_3 + IO + O_2 \quad (14)$$

1.1.3 Methyl iodide decomposition with gamma radiation

Tang *et al.* [7] proposed a mechanism for the radiolytic destruction of CH_3I which involved reaction with an activated species:

$$CH_3I + M^* \rightarrow CH_3\cdot + I\cdot + M \quad (15)$$

It is a reasonable assumption that the γ-ray energy is primarily absorbed by air to form active particles, M*, which in turn transfer energy to CH_3I molecules upon collision.

It is generally accepted that the reaction of methyl radicals with oxygen takes place *via* two routes, namely, thermomolecular reaction leading to the formation of methyl peroxide radicals

$$CH_3\cdot + O_2 + M \rightarrow CH_3O_2\cdot + M \quad (16)$$

and bimolecular reaction which gives rise to formaldehyde

$CH_3\cdot + O_2 \rightarrow HCHO + OH\cdot$ (17)

I_2 is formed by recombination of I·:

$I\cdot + I\cdot + M \rightarrow I_2 + M$ (18)

The last reaction accounts for the formation of I_2 observed in the experiments at high CH_3I concentrations, but would be unlikely to occur at low concentrations where other reactions of I· would be more likely.

2 Experiments

The project, NROi-3, was divided into two experiment series, 1. A further investigation of the behaviour of methyl iodide exposed to ozone and/or UV radiation in dry and humid air, 2. Investigation of the behaviour of methyl iodide in a strong gamma field. The experiments in sub-project 1 were performed at VTT in Finland, with the same experimental set-up, the EXSI-facility, which was used in previous experiments [3, 4, 5, 6]. The experiments in the second part of the NROI-3 project were performed at Chalmers University of Technology in Sweden. The set-up used in these experiments was partially taken from the EXSI-facility, but also a gamma radiation source was included to the system.

2.1 Experiments sub-project 1

The EXSI set-up (Facility for EXperimental Study of Iodine chemistry) is shown in Figure 1. and has been extensively described elsewhere [3, 4, 5, 6]. Therefore, it will just be briefly described here. The design of the facility is based on the sampling system manufactured previously at VTT [13].

The facility consists of several parts, where the methyl iodide production unit is the first part in the transport line. Methyl iodide vapour is transported to the UV-furnace by a stream of air. In some of the experiments this stream consisting ppm levels of ozone and/or varying concentrations of humidity. Ozone is produced from an external and adjustable ozone generator. The gas mixture is then transported through a glass tube of fused silica in the UV-furnace, where it is exposed to UVC-light from four UV-lamps.
The gas mixture and eventual formed particles is transported to the sampling furnace, where the stream was divided into four lines for analyzes of the mixture. The first line is the FTIR-line (Fourier Transform Infra Red), where the methyl iodide and the ozone concentrations are measured as well as the concentration of reaction products like methanol and formaldehyde.
The second line is the aerosol line, which consisted of several analysis instruments for measuring the formed aerosols. These instruments are CPC (Condensation Particle Counter), SMPS (Scanning Mobility Particle Sizer), ELPI (Electrical Low Pressure Impactor) and TEOM (Tapered Element Oscillating. Microbalance).
The third line in the sampling furnace is the analytical line, which is sub-divided into three separate lines that could be switched open one at a time. Each of these lines is consisting of a particle filter and two gas washing bottles in series. This makes it possible to have three different conditions during one experiment. The particle filter is made of paper and it is used

for collection and determination of the amount of solid iodine. After the experiments the paper filters are placed in sodium hydroxide solutions and the iodine content in the solutions is 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. The iodine content in the gas washing bottles solutions was determined with ICP-MS after the experiments.
The fourth line consists of a particle filter with the outflow placed in a fume hood. This line is open when the three lines in the analytical line were closed.

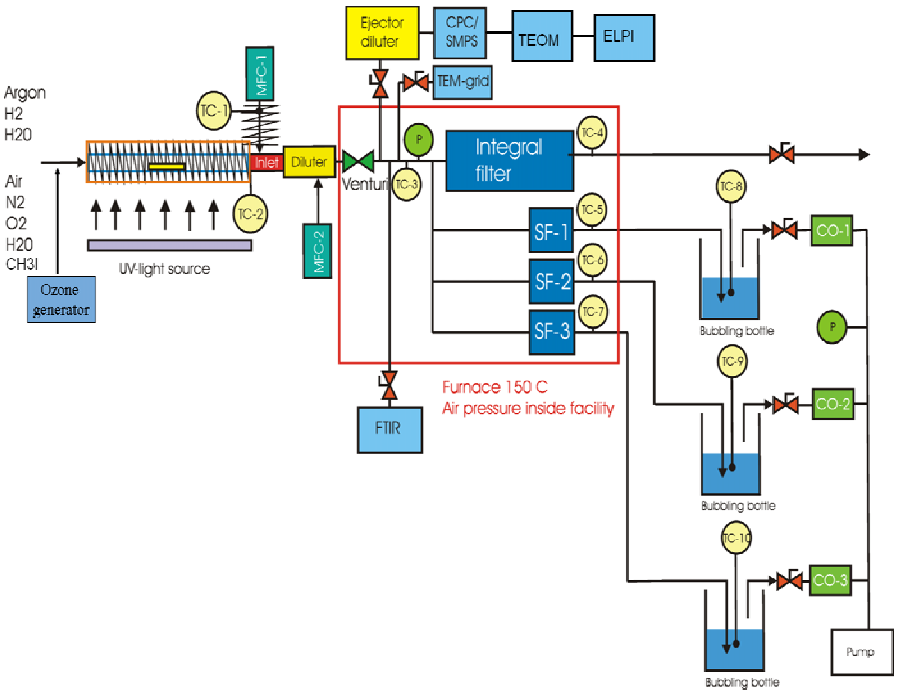

Figure 1: A schematically sketch of the experimental facility used for the experiments.

In total six experiments were performed and the experimental matrix can been seen in Table 1. In these experiments, the gas flow is transported through on of the lines with particle filter and gas washing bottles. Additional experiments were performed when further parameters were investigated, but there no data is given from the analytical line.
The parameters, which were investigated in the experiments, were the temperature, the ozone concentration, the UV-radiation intensity, the methyl iodide concentration and the humidity.

Table 1: The experimental matrix of the first sub-project.

Exp.	Atmosphere	Humidity	Total flow (l/min)	Flow through water bath (l/min)	Temperature (° C)	UVC-levels	Ozone level
1a	Air	No	6	0	120	4	10
1b	Air	No	6	0	120	4	5
1c	Air	No	6	0	120	4	1
2a	Air	No	6	0	90	4	10
2b	Air	No	6	0	90	4	5
2c	Air	No	6	0	90	4	1
3a	Air	No	6	0	50	4	0
3b	Air	No	6	0	50	2	0
3c	Air	No	6	0	50	0	0
4a	Air	Yes	6	1	120	4	0
4b	Air	Yes	6	2	120	4	0
4c	Air	Yes	6	3	120	4	0
5a	Air	Yes	6	1	120	4	1
5b	Air	Yes	6	2	120	4	1
5c	Air	Yes	6	3	120	4	1
6a	Air	No	6	0	120	4	1
6b	Air	No	6	0	120	4	5
6c	Air	No	6	0	120	4	10

2.2 Experiments sub-project 2

The facility used in the experiments was a modification of the EXSI facility and it is presented in Figure 2. The facility was connected to a gamma cell placed at Chalmers. The source of gamma radiation was ^{60}Co and the dose rate inside the cell was ~20 kGy/h. In these experiments the gamma cell replaced the UV furnace used in previous experiments [3, 4, 5, 6]. The inlet and outlet passages through the gamma cell were made of PEEK polymer. These flexible feed passages were needed, because the lines through the lid of the gamma cell were curved due to radiation safety issues. Other lines were made of stainless steel tubes with Sulfinert® coating, which has been used with success in all previous experiments [3, 4, 5, 6]. The heating of all lines was conducted with heating bands instead of a furnace. The temperature was set to 50 °C in all experiments. This temperature was chosen because the temperature inside the gamma cell was 50 °C and to get similarity between these experiment and those performed at VTT. The heat inside the gamma cell was produced because of high radioactive energy absorbed in the ambient lead shield.

The online measurement devices used in experiments were Condensation Particle Counter (CPC), Tapered Element Oscillating Microbalance (TEOM) and Fourier Transform Infra Red (FTIR). They were used to analyse the concentration of aerosol particles, the aerosol mass concentration and the concentration of gaseous compounds respectively. FTIR was also used to identify the gaseous compounds.

The facility was also equipped with analysis filters and trapping bottles for solid iodine and gaseous iodine samples, respectively.

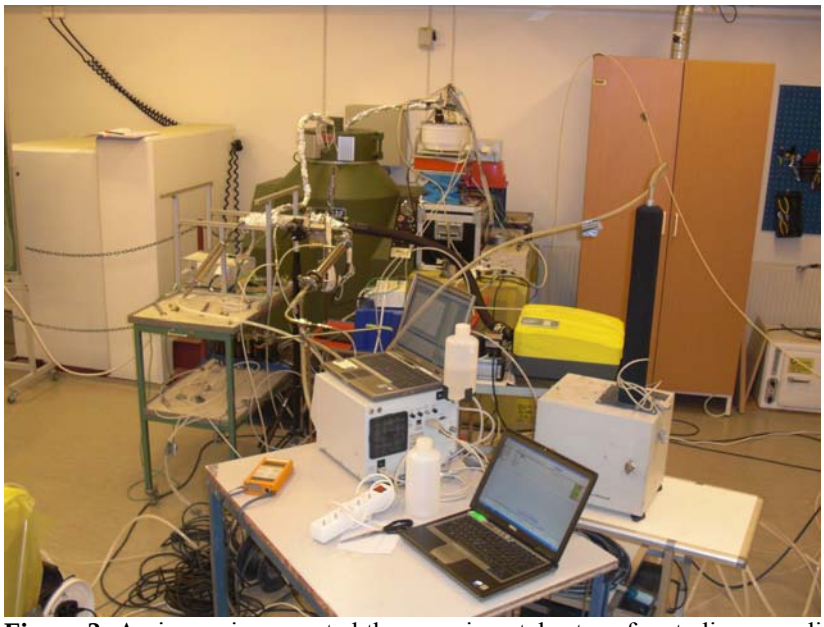

Figure 2: An image is presented the experimental set-up for studies on radiolytical oxidation of gaseous methyl iodide by gamma radiation.

The experimental matrix of the second sub-project can be seen in Table 2. Several parameters were changed in the six experiments, among others flow rate, humidity and iodine precursor.

Table 2. The details of experiments on radiolytical oxidation of CH_3I by gamma radiation in air.

Exp.	Temperature [°C]	Total flow rate [l/min]	Atmosphere	Other
1A	50	2, 4, 6	dry/humid	Ozone formation
1B	50	2, 4, 6	dry/humid	Ozone formation
1C	50	2, 4, 6	dry/humid	Ozone formation
2A	50	2, 4, 6	dry/humid	CH_3I feed
2B	50	2, 4, 6	dry/humid	CH_3I and O_3 feed
2C	50	2	dry/humid	CH_3I, C_2H_5I and O_3 feed

3 Results and discussion of sub-project 1

This part was a continuation of previous experiments in NROI-2. The aim was to investigate the effect of exposing ozone and/or UV-radiation to methyl iodide and also the effect of humidity. In this report the results from the NROI-2 project is also presented, to give a more total view of the radiolytic oxidation of organic iodine in severe accident conditions. However, the main results from the experiments done in NROI-3 are presented in Table 3. The presented results in this chapter are here divided into the dry and the humid experiments.

Table 3: The main result of the experiments in NROI-3.

Exp.	CH_3I concentration (ppm)	Particle concentration (#/cm3)	Particle size (nm)	Particle mass (ng)	Moles of iodine particles/Moles of iodine gas
1a	-	2.8E+08	128	397	0.0189
1b	-	1.2E+08	176	352	0.2230
1c	-	6.8E+07	192	113	0.0098
2a	2581	1.2E+08	131	166	0.0445
2b	2700	1.2E+08	174	236	0.1788
2c	2868	6.8E+07	177	83	0.0523
3a	3545	6.4E+07	103	5	0.0016
3b	3565	4.8E+07	70	1	0.0004
3c	3627	3.3E+03	44	0	0.0002
4a	2841	7.3E+07	106	4	0.0005
4b	2768	5.1E+07	99	2	0.0003
4c	2693	3.8E+07	91	1	0.0078
5a	1624	1.0E+07	185	31	0.0032
5b	1435	1.8E+06	183	3	0.1135
5c	1188	5.2E+06	185	14	0.4638
6a	2909	7.0E+07	196	178	0.0363
6b	2525	9.5E+07	197	381	0.2198
6c	1044	7.7E+07	172	480	0.4315

3.1 Dry experiments

Several different conditions were investigated in the dry experiments, like temperature variation, varying of UV-radiation and ozone concentration, change residence time etc.

3.1.1 Particle Formation

The particle formation was instant and extensive when methyl iodide was exposed to ozone and/or UV-radiation in all different conditions. No particles were formed when only methyl iodide was present in the system.

As can be seen in Figure 3a-c the particle mass concentration is increasing with both increased ozone concentration and UV-radiation intensity. When the UV-field is activated, but no ozone is present in system, the particle mass concentration is just slightly higher than conditions where only CH_3I is present in the system. But, when also ozone is present the particle mass concentration is increasing extensively, especially at high ozone concentrations. The particle mass concentration is significant higher when ozone and UV-radiation are present, compared with only ozone in the system. This is true for the experiments performed at 50 ºC and 90 ºC, but at the 120 °C the temperature effect seems to be dominating in the particle formation process. As has been declared about the reaction mechanisms in chapter 1.1, this is rather logical that the particle mass concentration is increasing when ozone is present and the UV-field is activated. Methyl iodide is decomposed to two radicals, a methyl group and an iodine atom, by UV radiation. Then ozone is used to oxidize the iodine atom to

iodine oxides (I_xO_y), iodine particles. Ozone can by itself also split the methyl iodide molecule, especially at elevated temperatures, and if ozone is in excess the formation of iodine particles (I_xO_y) is possible. Thus, the more ozone is present in the system the heavier mass, bigger molecules, of the formed particles.

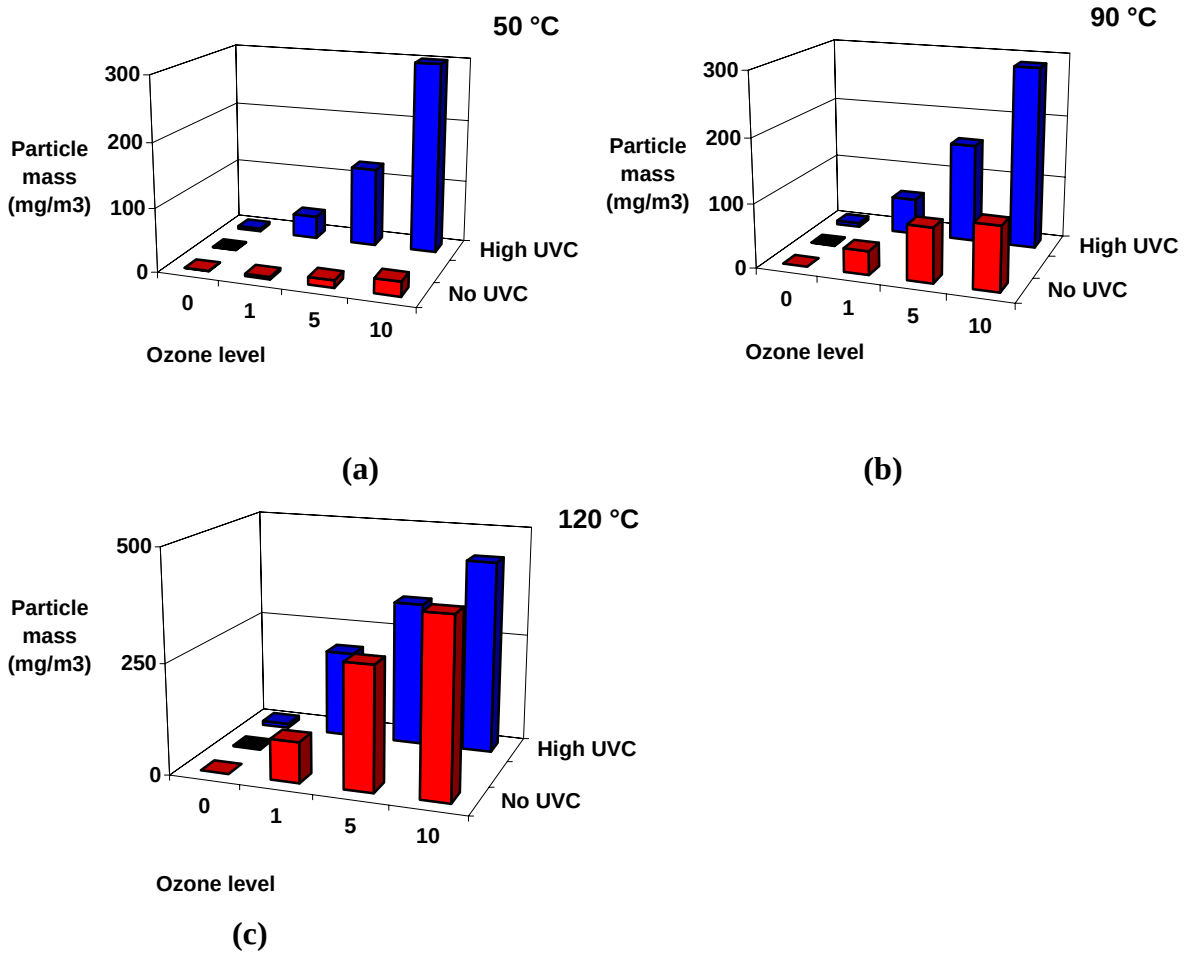

Figure 3a-c: The particle mass at different temperatures, UV-intensities and ozone levels.

The trends about the particle concentration are not as clear as for the particle mass, when the parameters temperature, UV-intensity and ozone concentration are varied. The particle concentration seems to increase with increased ozone concentration, which can be seen in Figure 4a-c. This trend is obvious when the UV-radiation is also present in the system. However, the particle concentration does not seem to increase due to present of UV-radiation at the same ozone level. This depends on that the particle size is larger in experiments with UV-radiation, thus the particles are bigger but fewer (Figure 5). This can depend on the fact that ozone, instead of be used for breaking the CH_3I molecule, can been able to oxidize the formed I-atoms to form iodine oxides. The splitting of the methyl iodide molecule is occurring due to the UV-radiation in these experiments, which can see in chapter 1.1.

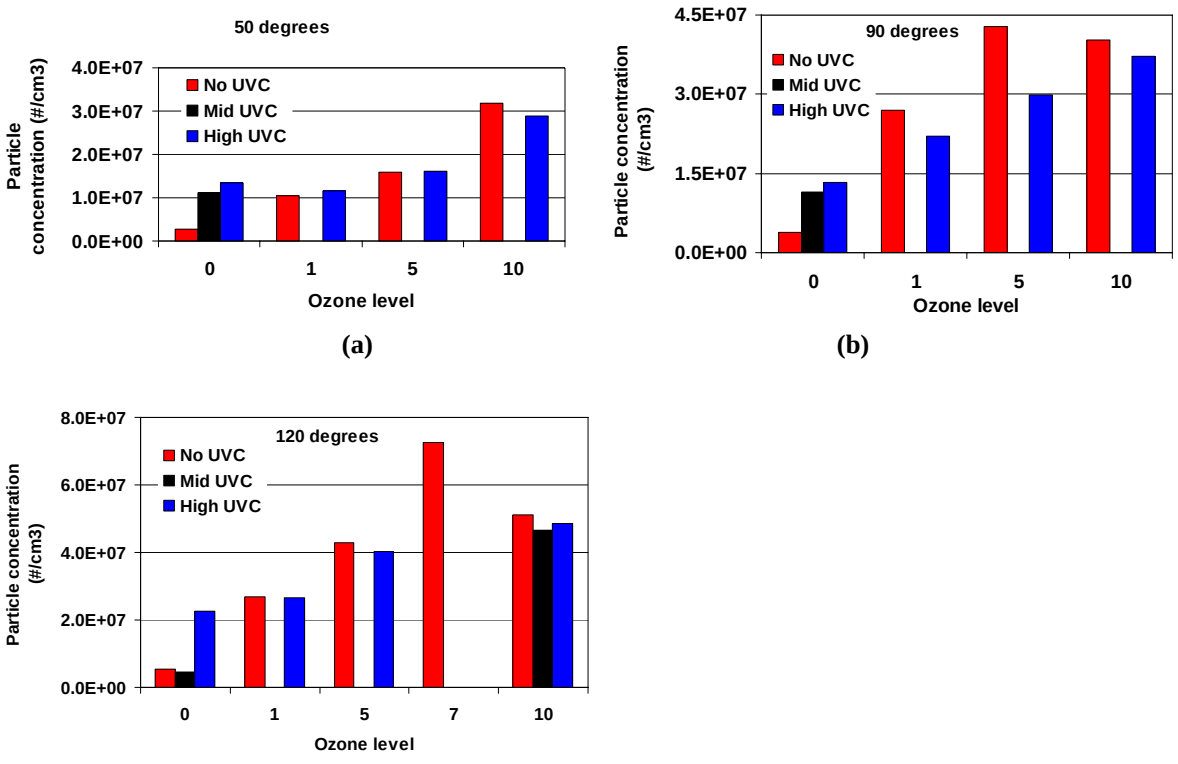

Figure 4a-c: The particle concentration in the dry experiments at different temperatures, UV-intensities and ozone concentrations.

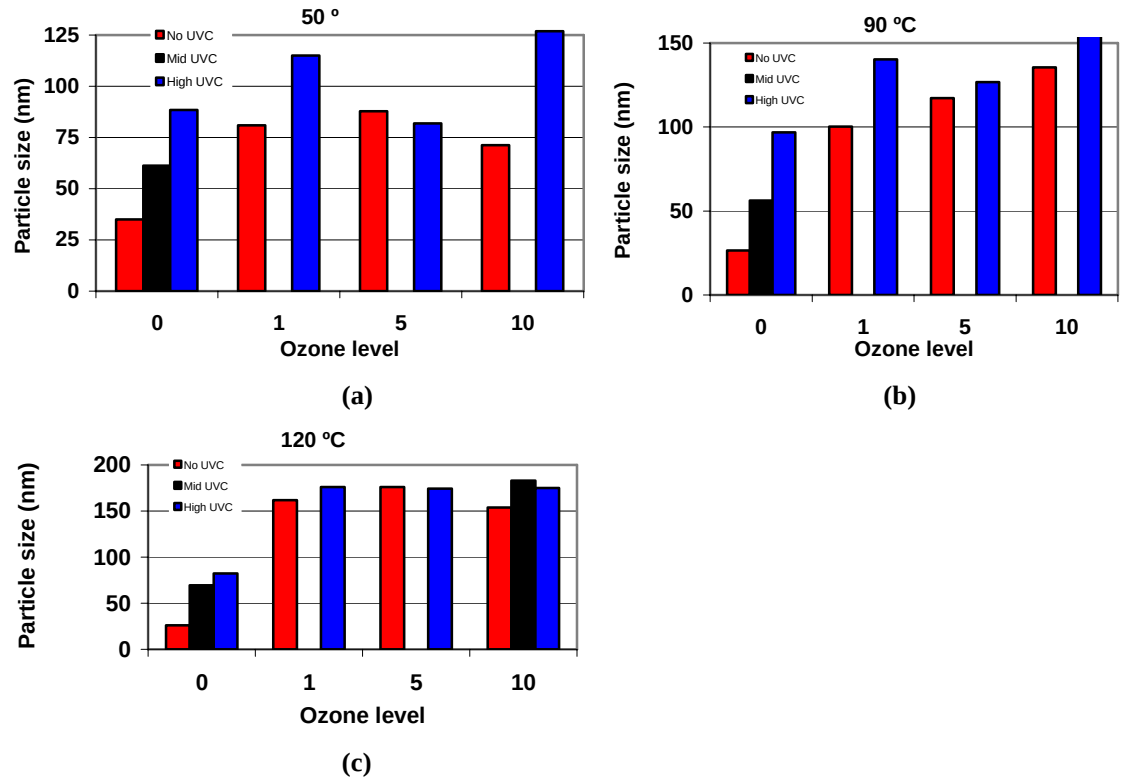

Figure 5a-c: The plots are showing the size of the particles at different temperatures, UV-intensities and ozone concentrations.

The variation of the particle size is even more difficult to understand and explain. The particle size seems to reach a maximum level independent of the ozone concentration. The size of the iodine particles is varied between 75 nm and as maximum 175 nm. However, the temperature seems to be a more important parameter affecting the size of the particles. The particle size is increasing with the temperature. In most of the data points the particle size is increasing when UV-radiation is present in the system.

3.1.2 The speciation of the particles

The speciation of the formed particles, the iodine oxides, was investigated during NROI-2. From these experiments it was possible to make conclusions that the particles were some kind of iodine oxides, presumably I_2O_5 or I_4O_9, which was determined with SEM-EDX. A more accurate determination of the speciation of the particles was not possible to do, because the particles were melted and fused together under the electron beam. Similar behaviour of the particles were shown with measurements with other analysis methods like TEM. However, the SEM-EDX measurements shown that the particles only contained oxygen and iodine atoms. This was true also for the humid experiments.

3.1.3 ICP-MS analyses

Unreacted methyl iodide and other gaseous iodine species were trapped in gas washing bottles, which was described in chapter 2.1. Besides, the formed particles where trapped at special paper filters. The iodine content in the gas washing bottles solutions and on the paper filters were analyzed with ICP-MS. The results from these measurements made it possible to compare the ratio between iodine aerosols and gaseous iodine in the gas stream.

As can be seen in Figure 6, the iodine aerosols/gaseous iodine ratio is increasing with increasing ozone level. This means that amount of iodine particles is increasing and the amount of total gaseous iodine is decreasing. Similar results can be seen in Figure 7, which showing the iodine aerosols/gaseous iodine ratio at different ozone concentrations when the UV-field is activated in the system. But, these data are not as obvious as the results with no UV-radiation present in the system. There was not either an obvious temperature effect on the particle/gas ratio, which can be seen in Figure 7.
One conclusion that can be made from the ICP-MS data is that the ratio between iodine aerosols and gaseous iodine is never exceeding 1, nevertheless the condition in the system. This means that the number moles of gaseous iodine are always larger than the moles of iodine particles. Compared to the experiment in the NROI-1 project, when elemental iodine (I_2) was used as precursor, there were several conditions when the amount of particular iodine was higher than the amount of gaseous iodine. Thus, the results in the NROI projects are showing that the radiolytic oxidation and transformation of gaseous (inorganic or organic) iodine to solid iodine oxides is more significant when inorganic iodine (I_2) is used as precursor.
The ICP-MS measurements are rather uncertain, due to severe memory effects can appear when iodine is measured.

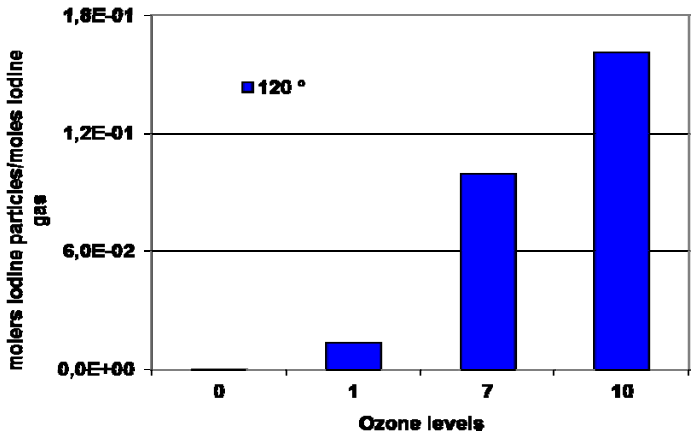

Figure 6: The ratio between the amount iodine particles and iodine gas at different ozone concentrations in the system. No UV-radiation is present in the system.

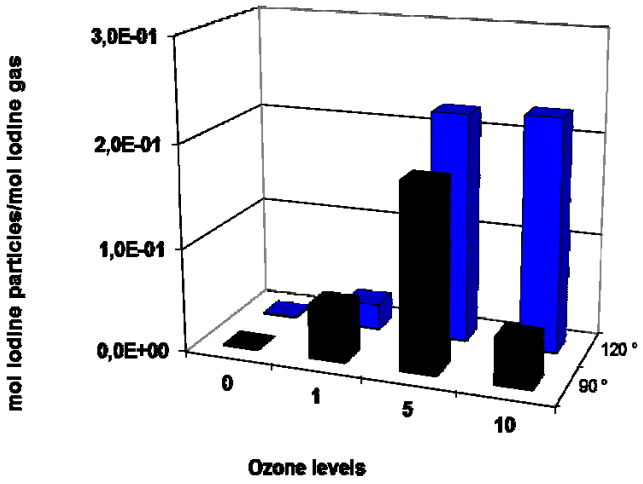

Figure 7: The ratio between the amount iodine particles and iodine gas at different ozone concentrations in the system at maximum possible UV-radiation intensity.

3.1.4 Gaseous reaction products

The speciation and quantification of the gaseous reaction products were measured with FTIR. Unfortunately, it was not possible to detect any possible formation of elemental iodine, I_2, because the analysis method cannot detect homonuclear diatoms. However, the concentration of methyl iodide and ozone was possible to follow and analyze during the experiments, even if the analyses of the data were sometimes difficult to analyse. Therefore a FTIR specialist was used to interpret the experimental data.

3.1.4.1 The methyl iodide concentration

The influence of several parameters, like ozone concentration and temperature, on the methyl iodide concentration in the system was investigated. As can be seen in Figure 8a-c, the temperature effect was significant in system. The concentration of CH_3I was always higher

than 4200 ppm at 50 °C, but not higher than 3000 ppm at elevated temperatures regardless the ozone concentration and the UV-radiation intensity in the system. At 50 °C the variation of the methyl iodide concentration was difficult to see at different ozone concentration and UV-radiation intensities. The methyl iodide concentration was more or less stable regardless ozone concentration and UV-radiation intensity. This was rather unexpected, because of significant particle formation when methyl iodide together with ozone and/or UV-radiation was present in the system. However, the low temperature in the facility during these experiments generated problems in the FTIR analyses. The FTIR device needed to be heated to at least 70 °C, which was 20 °C higher than the temperature in these experiments. This was done to reduce the negative influence of water vapour on the measurements. The heating temperature of the FTIR was chosen to be 70 °C. Thus, this relative low temperature can be the reason of the strange results because of increasing possibility of condensation of CH_3I on the tubes inside the FTIR. This makes is also possible that the real concentration of methyl iodide in system in these experiments was even higher.
Another explanation of the unexpected results may be that in these experiments the particle formation origin from the reactions between ozone and deposited iodine on surfaces in the facility. The heterophasic reactions (gas-surface) are governing at low temperature, but at elevated temperatures the homophasic reactions (gas-gas) are governing. At elevated temperatures the particle formation is extensive and the CH_3I concentration is more dependent on the ozone concentration compared to lower temperatures. But, the accumulation of methyl iodide on the surfaces in the system can also be more significant at elevated temperatures, thereof the lower detected concentration of methyl iodide in these experiments. However, the facility was cleaned after all experiments, but no significant differences of the amounts of iodine deposits on the tube walls were able to see.

The results for the experiments at elevated temperatures, 90 °C and 120 °C, are showing in general a significant lower concentration of CH_3I in the system. However, the results for the elevated temperatures were still quite inconsistent, especially in the experiments at 90 °C. When only UV-radiation is present, the methyl iodide concentration is decreasing with increasing UV-intensity as expected. The addition of ozone to system reduced the methyl iodide concentration, compared with only CH_3I presence. However, it seems that the amount of methyl iodide is increasing when both ozone and UV-radiation are present in the system. The inconsistent of the results of the 90 °C experiments can also depend of to low heating temperature (90 °C), with following of non unimportant condensation of methyl iodide on the surfaces inside the FTIR device.
The results of the 120 °C experiments are more consistent and easier to explain. The methyl iodide concentration is decreasing with increasing ozone concentration and UV-radiation intensity. Especially when the UV-field is activated, the methyl iodide concentration is linear declining to the ozone concentration. Thus, methyl iodide is decomposed and converted to iodine oxide particles and other gaseous reaction products.

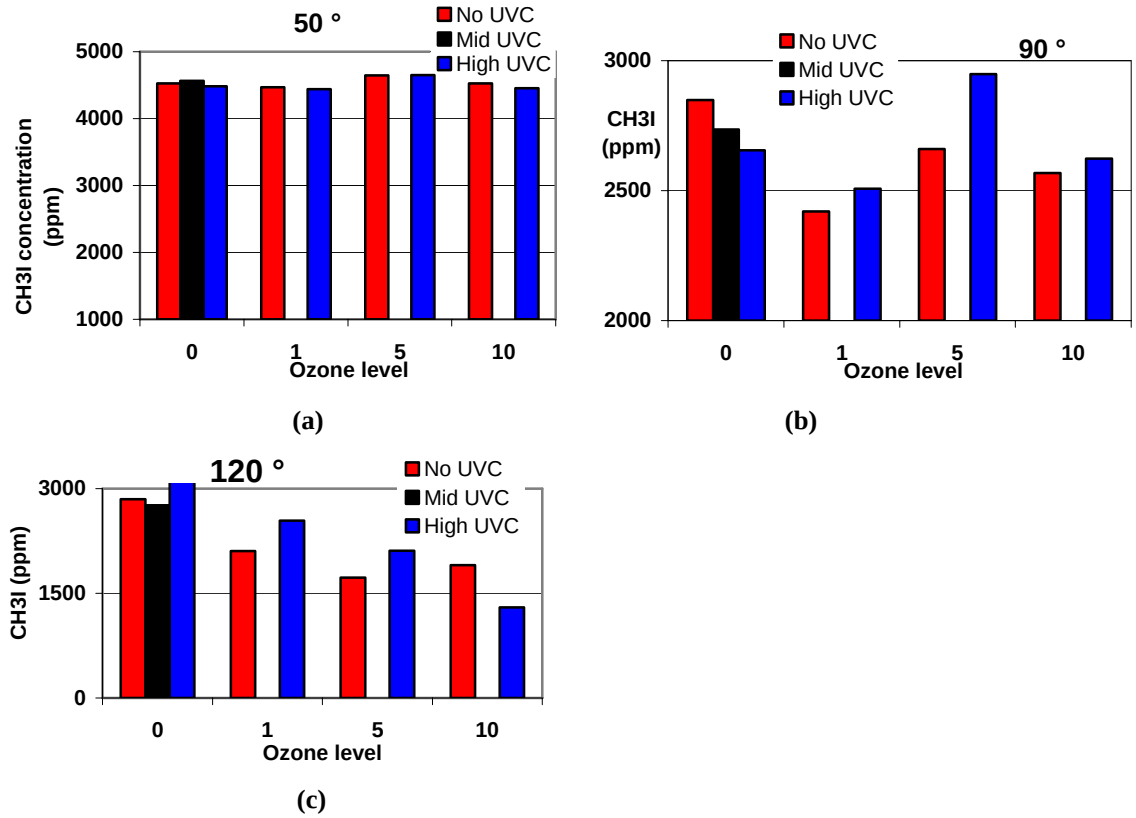

Figure 8a-c: The methyl iodide concentration at different temperatures, ozone levels and UV-radiation levels.

3.1.4.2 Other gaseous reaction products

The main reaction products formed in the reaction between O_3 and CH_3I with/without presence of UV-radiation were formaldehyde (CH_2O) and methanol (CH_3OH). These reaction products are not presence in system in system when no UV-radiation and/or ozone are present in system. Thus, an elevated temperature is not enough to decompose methyl iodide and form these reaction products. The concentration of methanol and formaldehyde is varied between 50 ppm to 700 ppm at high levels of ozone.
These results are consistent with the theory presented in chapter 1.1.

3.2 Humidity experiments

In some of the experiments the gas mixture was mixed with a flow (with varied flow rates) of moisture air, so the reaction inside the UV-furnace took place in humid conditions. The particle formation in these experiments was even more extensive when methyl iodide was present together with ozone and/or UV-radiation. When either the UV-field was activated or ozone was present, the particle formation was considerably more significant in humid conditions compared to dry conditions. This was true for the mass, the concentration and the size of the particles. At high ozone concentrations severe problems with clogging of the tubes of the analysis where appearing. Unfortunately, this resulted in some missing data points, especially for the measuring of the particle mass with the TEOM device. Particle masses as high as 1200 mg/m^3 were measured.

3.2.1 Particle formation

The size of the particles was larger when the experiments were performed in humid atmosphere compared to dry atmosphere; an example can be seen in Figure 9. As has been mentioned before the results were not particularly unexpected because of clogging of the tubes in humid conditions. The particles can be supposed to condensate on the water vapour, or reverse, which make the particles even larger.
The particle concentration is following similar behaviour as for the experiments with dry conditions, *i.e.* it is decreasing with increasing ozone concentration. The particles are growing and agglomerates.

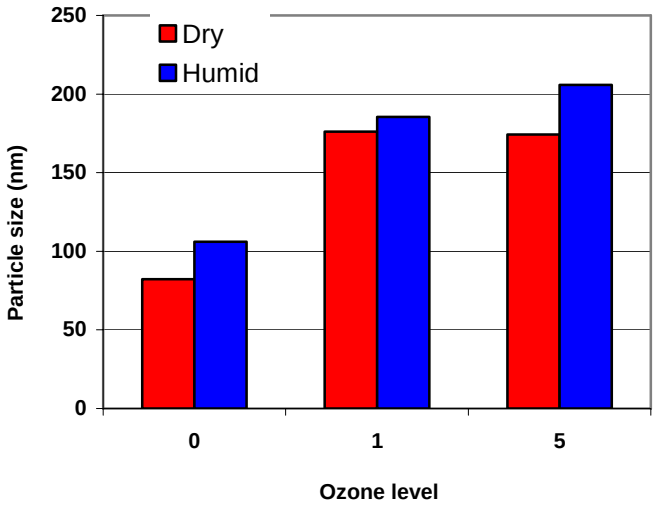

Figure 9: The particle size dependent on ozone level at both dry and humid conditions. An UV- field is activated in these conditions.

3.2.2 ICP-MS analyses

The outcome of analyses of the trapping solutions from the experiments with humidity in the atmosphere can be seen in Figures 10-11. Compared to dry conditions the ratio between iodine aerosols and gaseous iodine is increasing in humid conditions, especially at high ozone levels. High ozone levels and humidity are the only conditions when the particle/gas ratio is higher than 1, *i.e.* there is more moles of iodine aerosols than gaseous iodine in the system. When the humidity was varied in some of the experiments, the iodine particle/gas ratio is increasing with increasing humidity.

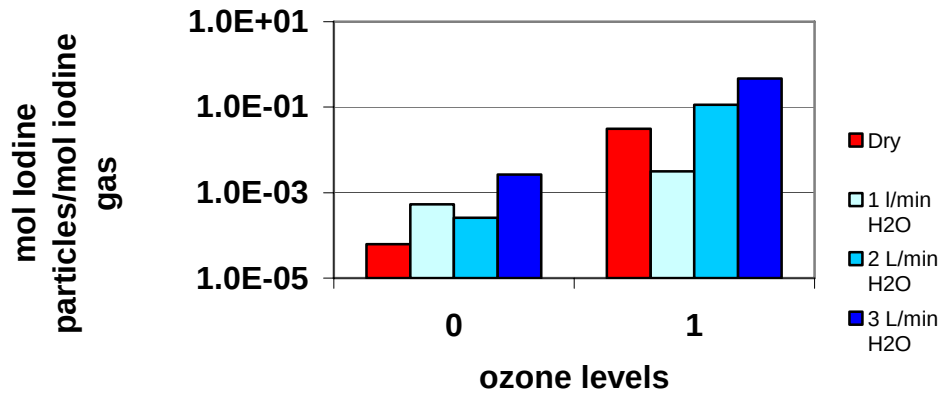

Figure 10: The figure is showing the iodine particle/iodine gas ratio at different humidity conditions with or without ozone present. UV-radiation is present in all conditions.

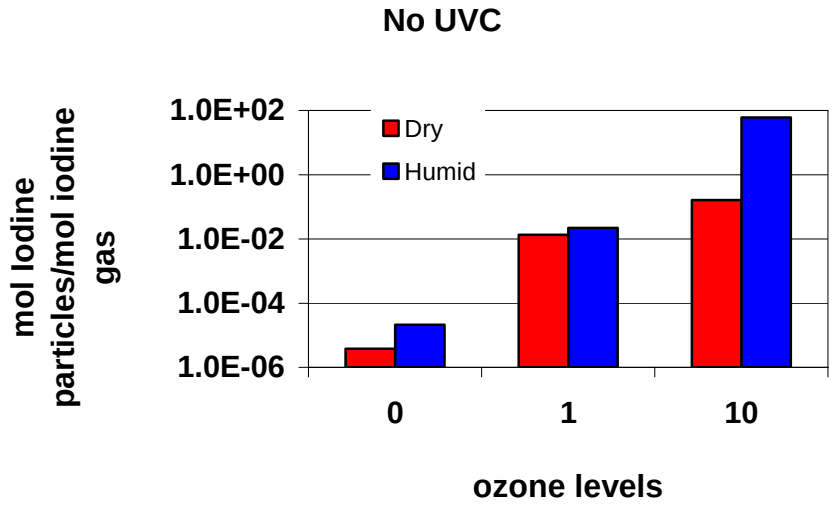

Figure 11: The figure is showing the iodine particle/iodine gas ratio at different ozone levels in dry or humid conditions.

3.2.3 Gas reaction products

Humid conditions in the experiments resulted in a lower concentration of methyl iodide compared to dry conditions, especially at high ozone levels and UV-radiation present. This is illustrated in Figure 12. The concentration of CH_3I is as much as factor of tenth lower in humid conditions at the highest ozone levels. When the UV-field is not activated the influence of humidity on the reduction of the methyl iodide concentration is not obvious. Therefore, the conclusion can be made that some kind or radiation has to be present to get an additive effect of CH_3I concentration from humidity.

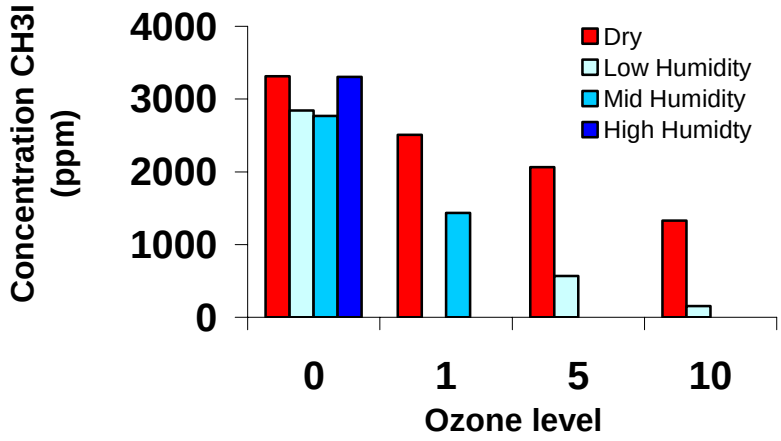

Figure 12: The methyl iodide concentration at different ozone levels at dry or humid conditions. UV-radiation is present in system in all conditions.

4 Results and discussion of sub-project 2

The outcome of the experiments was not as consisted and accurate as was planned and hoped. Only some of the data of the CH_3I behaviour in a gamma radiation field are presented in this report, because the data is rather uncertain.

4.1 Ozone formation in air by gamma radiation

The ozone sample was taken at the outlet of gammacell. As a result, no ozone was detected with FTIR in any experiment. The radiation dose for air sample inside the gamma radiation field was only ~10 Gy. That is due to short residence time (maximum ~2 seconds) inside the cell. FTIR detects gaseous compounds in ppm scale and according to Funke the concentration of ozone formed within the residence time is in ppb scale [12]. Therefore, the concentration of ozone was too low to be measured with FTIR connected to this set-up with already described conditions.

4.2 Gaseous reaction products of CH_3I radiolysis

The measured gaseous reaction products formed in experiment 2A are presented in Figure 13. In the experiment the feed of methyl iodide (0.1 l/min air saturated with CH_3I at 30°C) was started at 45min. The total flow rate increased from 2 to 4 l/min at 1h 40min and from 4 to 6 l/min at 2h. The injection of water was started at 2h 15min at which time also the flow rate was decreased again back to 2 l/min. The total flow rate through the facility was increased to 4 l/min at 3h and to 6 l/min at 3h 20 min. As a result of oxidation of gaseous CH_3I by gamma radiation, a few gaseous reaction products were detected with FTIR. Formaldehyde (HCHO) was formed as expected. However, the formation of iodoform (CHI_3) was a new result, compared to the results from experiments with the experiment with UV-radiation present. The amount of gaseous reaction products species was very low compared to UV experiments. Observed differences might be due to low amount of ozone produced by gamma radiation and

radiation type itself. It should be noted though that for some reason essentially no CH_3I was detected in the facility.

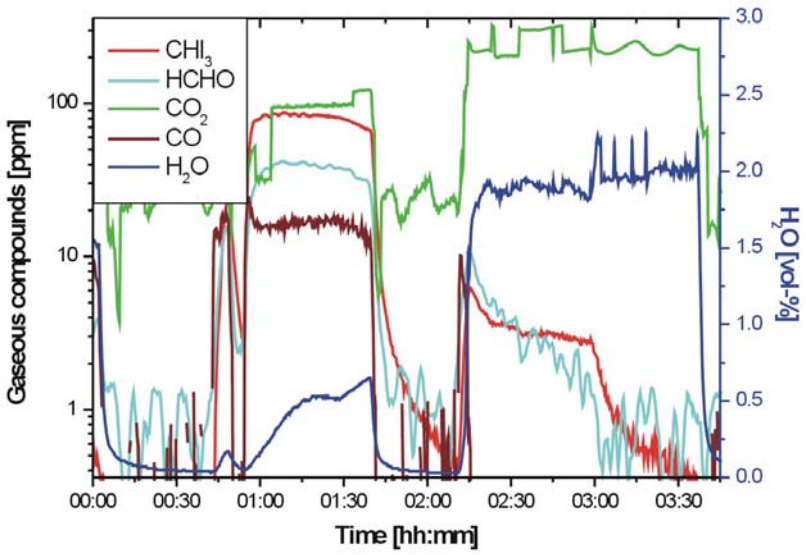

Figure 13: In figure are presented the gaseous compounds measured with FTIR in experiment 2A. Gaseous CH_3I has been exposed to gamma radiation at dry and humid conditions. These results are preliminary and the reference of CHI_3 in FTIR analysis will be updated. However, it can be seen that the main gaseous reaction products were formaldehyde (HCHO) and iodoform (CHI_3).

In experiment 2A aerosol and gaseous samples were collected with plane filters and trapping bottles respectively. These devices were overheated in that experiment and it was not possible to have more than two gas samples in experiment 2A. Because of to high temperature, errors in heating bands, these devices broke down and they could not be used in the other experiments. However, it was seen during the sampling in experiment 2A that there was a very strong generation of (white) vapour in the trapping bottles, which is illustrated in Figure 14. This has also been noticed in previous experiments, where methyl iodide has been introduced into a stream of high ozone concentrations.

Figure 14: The formation of white vapour in two bottles can be seen.

4.3 Aerosol reaction products of CH_3I radiolysis

Some of the measured gaseous species and aerosol particles number concentration in experiment 2C are presented in Figure 15. The feed of methyl iodide started at 1h and it was stopped at 1h 25min. The injection of water started at 1h and it reached stable level at 1h 5min. The feed of ozone started at 1h 13 min and it was stopped at 1h 36min. The formation of aerosol particles was depended on the concentration of ozone. The concentration of particles was measured with CPC directly from sample flow without dilution. The stream to the CPC device always needed a dilution in the experiments with UV-radiation and/or ozone present, because of to high production of particles.

However, the formation of aerosol particles was very high when ozone was produced form the ozone generator. An example of measurement carried out in experiment 2C is presented in Figure 15. It can be seen that when the concentration of ozone increases the concentration of aerosol particles increases at the same time. The number concentration of particles exceeded the measurement range of CPC. High ozone concentration may have caused decomposition of CH_3I and subsequent formation of IO_x particles. Particle concentration decreased by at least two orders of magnitude, when methyl iodide feeding was stopped. Thus, methyl iodide was transported through the system. However, very little gaseous decomposition products were measured.

The concentration of ozone slightly increased when CH_3I feed was stopped. There was likely no more consumption of these species in reactions with CH_3I and its reaction products.

The formation of aerosol particles was very low when ozone was produced only by air radiolysis with gamma radiation.

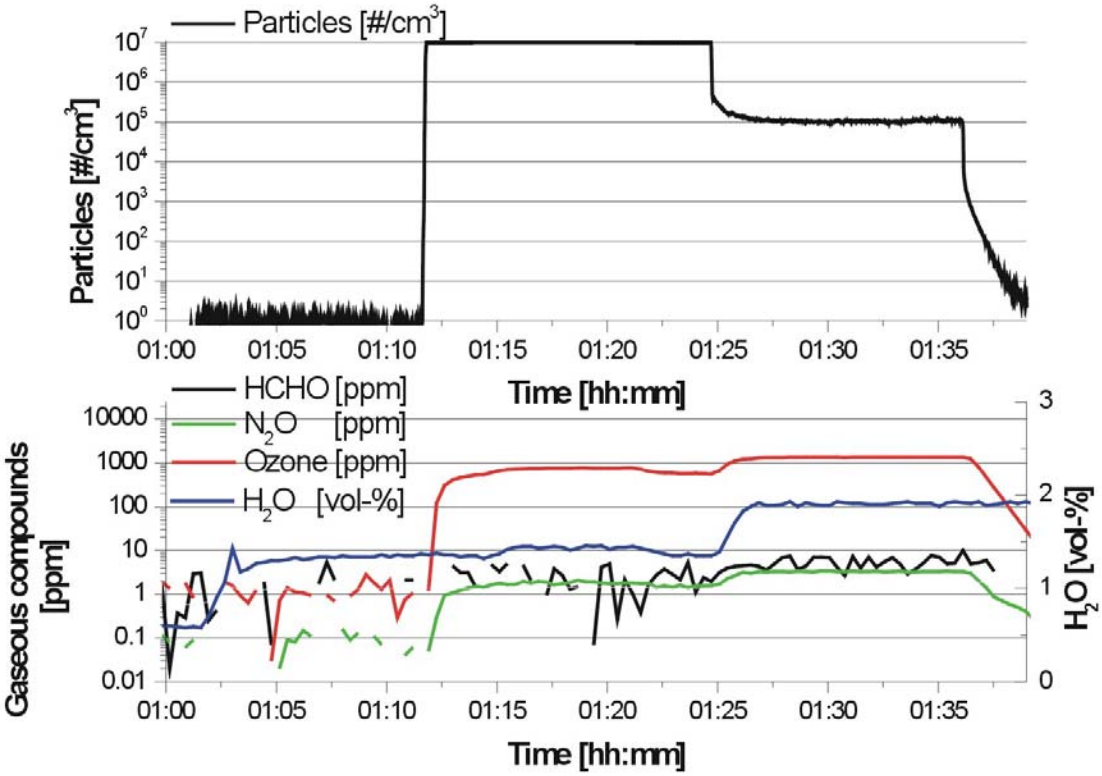

Figure 15: A sample of the measured gaseous species and aerosol particles number concentration in experiment 2C is presented.

5 Conclusions

5.1 Sub-project 1

An experimental study on radiolytic decomposition of methyl iodide in containment conditions was carried out at VTT in co-operation with Chalmers 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 main conclusions can be made from the results of the performed experiments within the NROI-2 and NROI-3 project:

- The methyl iodide concentration in the facility was reduced with increasing temperature, increasing UV-radiation intensity. Similar behaviour was seen when ozone was present in the system. This was true for both dry and humid conditions. When both UV-radiation and ozone were present in system, the reduction of methyl iodide was even more evident and especially in humid conditions.
- Formed organic gaseous 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 UV-radiation and/or when ozone is present. The production of particles was more extensive, when both ozone and UV-radiation was present in the system. The mass of the formed particles was between 20-500 mg/m^3 dependent on ozone concentration and UV-radiation intensity. At humid conditions the particle formation was even more extensive, especially at high ozone levels, which resulted in problems with clogging inside the facility tubes. It was possible to measure particle masses as high as 1200 mg/m^3 in some humid conditions.
- The size of the formed primary particles was about 10 nm and the size of secondary particles was between 50-200 nm. The size of the particles increased in humid conditions, but only when both ozone and UV-radiation were present in the system.
- From the ICP-MS measurements of the trapped particles on the particle filters and SEM-EDX analyses of the caught 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 during SEM-EDX analyses.
- The formation of particles when elemental iodine is used as precursor instead of methyl iodide is significant higher. In some conditions the ratio between iodine aerosols and gaseous iodine is higher than 1, when I_2 is used as precursor. This is not the case when CH_3I is used as precursor. This conclusion can be made by comparing the results from NROI-1 and NROI-2/NROI-3.

5.2 Sub-project 2

Some main conclusions can be made from the results from the second sub-project:

- The formation of ozone in air by gamma radiation was very low compared to the formation by UV-radiation. In these experiments the concentration of ozone formed by gamma radiation was below the detection limit (ppm scale) of FTIR. In order to produce higher ozone concentration, the residence time should be significantly longer.

- The transport of gaseous methyl iodide through the facility was much lower than expected. It is possible that CH_3I precursor was not in perfect condition, or the facility might have leaked at the inlet or severe adsorption of methyl iodide in system for some unknown reason.

- The amount of measured gaseous reaction product species was low compared to previous experiments with UV-radiation. Formaldehyde was detected as expected. The formation of iodoform (CHI_3) was an interesting result. That species has not been detected before in similar experiments.

- The concentration of aerosol particles formed by radiolytic oxidation of CH_3I was low. This is probably due to low production of ozone in gamma radiation. In some tests there was an additional ozone feed. As a consequence, a very high concentration of aerosol particles was measured.

This study was the first test with gamma radiation and therefore only preliminary results can be presented.

6 Acknowledgments

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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.

In year 2008 the NROI project, a Nordic collaboration studying iodine chemistry in the containment, was started. During year 2008 (NROI-1) the radiolytic oxidation of elemental iodine was investigated and during 2009 (NROI-2), the radiolytic oxidation of organic iodine was studied. This project (NROI-3) is a continuation of the investigation of the oxidation of organic iodine. The project has been divided into two parts. 1. The aims of the first part were to investigate the effect of ozone and UV-radiation, in dry and humid conditions, on methyl iodide. 2. The second project was about gamma radiation (~20 kGy/h) and methyl iodide in dry and humid conditions.

1. Experimental results showed that the methyl iodide concentration in the facility was reduced with increasing temperature and increasing UV-radiation 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.

The particle formation was instant and extensive when methyl iodide was exposed to ozone and/or radiation at all temperatures. The size of the formed primary particles was about 10 nm and the size of secondary particles was between 50-200 nm. From the SEM-EDX analyses of the particles, the conclusion was drawn that these were some kind of iodine oxides (I_xO_y). However, the correct speciation of the formed particles was difficult to obtain because the particles melted and fused together under the electron beam.

2. The results from this sub-project are more inconsistent and hard to interpret. The particle formation was significant lesser than corresponding experiments when ozone/UV-radiation was used instead of gamma radiation. The transport of gaseous methyl iodide through the facility was much lower than expected for some unknown reason. A “new” reaction product in this kind of experiments was detected, namely iodoform (CHI_3), but the data is rather uncertain.

Key words severe accidents, iodine, aerosols, methyl iodide, radiolytic oxidation

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