Ion recombination in liquid ionization chambers

Development of an experimental method to quantify general recombination

Jonas Andersson

I dedicate this thesis to my beloved family, Susanne and Sam.

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Abstract

An experimental method (the two-dose-rate method) for the correction of general recombination losses in liquid ionization chambers has been developed and employed in experiments with different liquids and radiation qualities. The method is based on a disassociation of initial and general recombination, since an ionized liquid is simultaneously affected by both of these processes.

The two-dose-rate method has been compared to an existing method for general recombination correction for liquid ionization chambers, and has been found to be the most robust method presently available.

The soundness of modelling general recombination in liquids on existing theory for gases has been evaluated, and experiments indicate that the process of general recombination is similar in a gas and a liquid. It is thus reasonable to employ theory for gases in the two-dose-rate method to achieve experimental corrections for general recombination in liquids. There are uncertainties in the disassociation of initial and general recombination in the two-dose-rate method for low applied voltages, where initial recombination has been found to cause deviating results for different liquids and radiation qualities.

Sensitivity to ambient electric fields has been identified in the microLion liquid ionization chamber (PTW, Germany). Experimental data may thus be perturbed if measurements are conducted in the presence of ambient electric fields, and the sensitivity has been found to increase with an increase in the applied voltage. This can prove to be experimentally limiting since general recombination may be too severe for accurate corrections if the applied voltage is low.

Key words: General recombination, initial recombination, liquid ionization chamber, radiation dosimetry

List of original papers and preliminary report

This thesis is based on the following papers, referred to by the respective Roman numerals in the text.

I.   Andersson J and Tölli H 2011 Application of the two-dose-rate method for general recombination correction for liquid ionization chambers in continuous beams *Phys. Med. Biol.* **56** 299-314

II.   Andersson J, Johansson E and Tölli H 2012 On the property of measurements with the PTW microLion chamber in continuous beams *Med. Phys.* **39** 4775-87

III.   Andersson J, Kaiser F-J, Gómez F, Jäkel O, Pardo-Montero J and Tölli H 2012 A comparison of different experimental methods for general recombination correction for liquid ionization chambers *Phys. Med. Biol.* **57** 7161-75

IV.   Andersson J and Tölli H 2013 A study of recombination losses in liquid ionization chambers *Submitted to Phys. Med. Biol.*

A preliminary report of findings in this thesis has been presented at the World Congress on Medical Physics and Biomedical Engineering May 26-31, 2012 Beijing, China

Andersson J and Tölli H 2012 The Use of Liquid Ionization Chambers in Radiation Dosimetry *IFMBE Proceedings* ISSN 1680-0737; 39

Abbreviations

2DR	Two-dose-rate method
2VM	Two-voltage method
3VM	Three-voltage method
CT	Computed tomography
EPR	Electron paramagnetic resonance
IAEA	International Atomic Energy Agency
IMRT	Intensity modulated radiation therapy
ISO	Isooctane
LIC	Liquid ionization chamber
NACP	Nordic Association for Clinical Physics
SSDL	Secondary standard dosimetry laboratory
STP	Standard Temperature and Pressure
TMS	Tetramethylsilane

Sammanfattning (Swedish)

För att kvalitetssäkra användningen av joniserande strålning inom sjukvården används vanligtvis jonisationskammare för att mäta den absorberade stråldosen i en given tillämpning. En sådan detektor bygger på att elektriskt laddade partiklar som skapats av den joniserande strålningens växelverkansprocesser samlas in med hjälp av ett pålagt elektriskt fält. Den uppmätta signalen från en jonisationskammare ska vara proportionell mot den absorberade stråldosen. Tillförlitligheten hos dessa instrument har genom omfattande arbete verifierats för användning inom medicinska tillämpningar med joniserande strålning.

Användning av joniserande strålning inom sjukvården för både terapeutiska och diagnostiska ändamål handlar idag ofta om tillämpningar med små och väl avgränsade strålfält. Exempel på sådana tillämpningar är intensitets-modulerad strålterapi för cancerbehandling och datortomografi, där röntgenstrålning används för tredimensionell avbildning av patienter för avancerad diagnostik. Användning av små och väl avgränsade strålfält är mycket fördelaktigt då den absorberade stråldosen till organ och vävnader utanför det behandlade eller avbildade området kan begränsas.

Den vanliga typen av jonisationskammare är inte väl anpassad för att göra mätningar i små och väl avgränsade strålfält, då den gasfyllda mätvolymen är förhållandevis stor vilket leder till att strålfält med skarpa gradienter återges på ett felaktigt sätt. Ett möjligt alternativ till den konventionella jonisationskammaren är här vätskejonisationskammaren, där vätska används istället för gas i den känsliga mätvolymen. Den känsliga mätvolymen i en vätskejonisationskammare kan vara mycket liten på grund av hög densitet och känslighet för joniserande strålning i vätska jämfört med gas. Dessa egenskaper leder dock även till problem med att tolka mätsignalen. På grund av hög känslighet och densitet kommer de skapade laddningsbärarna i en joniserad vätska i stor utsträckning förloras genom rekombinationsprocesser där bärarnas laddning reduceras. Mätsignalen från en vätskejonisationskammare måste korrigeras för sådana rekombinations-förluster för att dessa instrument ska ge ett mått som är proportionellt mot den absorberade stråldosen.

I det här arbetet har en experimentell metod utvecklats för att korrigera mätsignalen från en vätskejonisationskammare för rekombinationsförluster (paper I). Metoden är baserad på en separation av olika rekombinations-effekter, då de skapade laddningarna i en vätska kan rekombinera till neutrala molekyler på olika sätt. En vätskejonisationskammare (PTW

microLion, Tyskland) har använts för att utreda tillämpbarheten i olika strålkvaliteter och miljöer (paper II). Vidare har metoden som utvecklats i det här arbetet jämförts med en alternativ metod för korrektion av rekombinationsförluster i vätskejonisationskammare (paper III). Det finns idag ingen teoretisk beskrivning av rekombinationseffekter specifik för vätskejonisationskammare, och därför har tillämpbarheten av teori framtagen för gaser utvärderats för vätskor (paper IV).

Metoden för korrektion av rekombinationsförluster som utvecklats i det här arbetet möjliggör användning av vätskejonisationskammaren i medicinska tillämpningar för att utnyttja dess goda egenskaper. Vidare är metoden väl anpassad för användning i design av nya typer av vätskejonisationskammare, vilket är viktigt då olika tillämpningar exempelvis kräver kammardimensioner och vätskor av olika slag. Utöver tillämpningar för medicinsk strålningsfysik möjliggör det här arbetet även vidare studier av rekombinationsprocesser i vätskor.

1. Introduction

Present day medical applications involving ionizing radiation commonly employ narrowly collimated radiation beams for both therapeutic and diagnostic purposes, e.g. intensity modulated radiation therapy (IMRT) and computed tomography (CT). Narrowly collimated beams, and the associated highly modulated absorbed dose distributions in patient has an obvious beneficial effect in sparing absorbed radiation dose to organs and tissues outside the treated or investigated patient volume.

Air-filled ionization chambers are presently the most robust instruments available for radiation dosimetry in conventional clinical applications utilizing ionizing radiation (IAEA TRS-398 2000, IAEA TRS-457 2007). However, there are issues associated with employing conventional air-filled ionization chambers for radiation dosimetry in narrowly collimated beams, i.e. small field dosimetry, due to the large measurement volumes associated with these detectors. These precise and constricted radiation beams have steep gradients, and measurements with conventional ionization chambers will yield an insufficient spatial resolution in the resulting representation of the distribution of absorbed dose. A natural candidate for small field dosimetry would thus be the air-filled microionization chamber, given the proven robustness of the conventional chambers. However, the small measurement volumes required for these applications may affect the stability and signal to noise ratio of these chambers. There are several alternative dosimetric technologies that may be suited for small field dosimetry, for instance liquid ionization chambers (LICs), electron paramagnetic resonance (EPR) dosimetry, as well as diode and diamond detectors. However, there are disadvantages associated with all of these technologies, including deteriorating sensitivity with accumulated radiation dose, radiation quality dependence, stability issues and indirect readout of the measurement signal.

LICs may potentially become a valuable tool in modern radiation dosimetry, where highly modulated radiation beams are used, since these detectors can be manufactured with a small measurement volume compared to conventional ionization chambers. This is due to the high density and sensitivity to ionizing radiation of the liquid employed as the sensitive media. However, the high sensitivity of LICs also leads to substantial recombination of the charge created by ionization in the measurement volume, which yields a non-linear degradation of the resulting measurement signal. Furthermore, ion recombination in liquids consists of different processes, commonly separated into two categories as initial and general recombination. While loss of measurement signal due to recombination is

the primary obstacle for the usage of LICs, the performance of these detectors is also affected by radiation quality dependence, as well as a dependence on the temperature and possible non-negligible leakage currents.

To illustrate the difficulties in the interpretation of the measurement signal from a LIC, the formalism to express the absorbed dose to an ionization chamber sensitive media (D_m) can be analysed. This quantity can be related to the charge created in the sensitive media of an ionization chamber (Q), the mass of the sensitive media (m) and the detector efficiency, i.e. the average amount of energy required to form an ion pair in the media (W/e) as

$$D_m = \frac{Q}{m}\left(\frac{W}{e}\right). \tag{1.1}$$

For air-filled ionization chambers used in sparsely ionizing radiation beams, the ionization chamber charge reading is corrected for general recombination by an experimental two-voltage method (TRS-398, IAEA 2000) to determine the total amount of charge created. Furthermore, the efficiency of air-filled ionization chambers is well documented for applications in photon and electron beams $\left((W/e) = 33.97 \text{ J C}^{-1}\right)$. While the efficiency for air-filled ionization chambers is affected by the air temperature and pressure, this is trivially corrected for by normalization to STP (TRS-398, IAEA 2000). For LICs on the other hand, the quantities in (1.1) are not well known. Due to severe initial and general recombination, the charge reading from a LIC cannot be corrected for recombination losses by the two-voltage method. The efficiency of a LIC is also a source of uncertainty, since the measurement signal from an ionized liquid does not saturate in the same manner as that for air. An illustration of the saturation characteristics of a microLion LIC (PTW, Germany) containing isooctane compared to an air-filled Farmer chamber type 30010 (PTW, Germany) irradiated by continuous beams from a Cobalt-60 radiotherapy unit (alcyon II) is shown in figure 1.1.

microLion LIC, applied voltage (V)
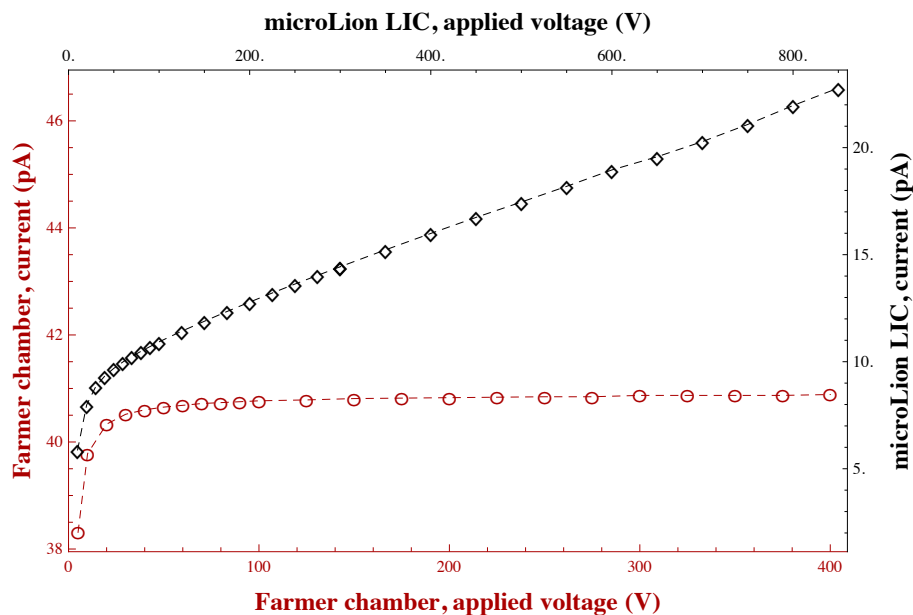
Figure 1.1. An illustration of saturation characteristics of air- and liquid-filled ionization chambers irradiated by continuous beams from a Cobalt-60 radiotherapy unit (alcyon II). The chambers used in the measurements are a PTW type 30010 Farmer air-filled ionization chamber and a PTW microLion LIC containing isooctane. The dashed line in each measurement series has been added to guide the eye of the reader.

As seen in figure 1.1, when the applied voltage is increased the air-filled ionization chamber readings saturates at a constant level, while the LIC readings continues to increase with the applied voltage. The reason for this curvilinear behaviour of the LIC readings is the presence of initial recombination. As the applied voltage, i.e. the collecting electric field strength, is increased the amount of the created charge escaping initial recombination will increase in a liquid. Initial recombination is negligible in air-filled ionization chambers employed for measurements in photon and electron beams, which is the reason why the two-voltage method can be used to correct for general recombination in these chambers. In order to correct the charge reading from a LIC for general recombination to achieve a proportional measure of the absorbed dose, initial recombination must thus be accounted for by theoretical or experimental means.

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1.1. Aims of the present work

The primary aim of the present work consisted of the development of a robust experimental method to quantify general recombination losses in liquid ionization chambers (LICs). To this end, a two-dose-rate method for general recombination correction for LICs employed in continuous beams has been developed (paper I). Given the variety of potential applications for LICs, a further objective was to investigate the performance of the method with a commercially available chamber (microLion, PTW Germany) with regard to dependence on radiation quality, as well as the robustness of this chamber design in different environments (paper II). Furthermore, the present work was also dedicated to a comparison of different methods for general recombination correction for LICs, including the two-dose-rate method, for both continuous and pulsed radiation beams (paper III). Due to the lack of dedicated theory to describe ion recombination in liquids, an aim of this work was also to investigate theory derived for gases to appraise the applicability for liquids commonly employed in LICs (paper IV).

2. Liquid ionization chambers

Liquid ionization chambers (LICs) are manufactured and operated in the same fashion as conventional air-filled ionization chambers, presently used as a reference instrument in radiation dosimetry. The principal difference is the sensitive media, which as the name implies consists of a nonpolar dielectric liquid instead of air. The microLion LIC type (PTW, Germany) employed in the present work is plane parallel, i.e. the electrodes and the chamber body encapsulate a cylindrical measurement volume. The measurement volume in this LIC design is defined by an electrode separation of 0.35 mm and a diameter of 2.5 mm. Furthermore, the microLion LICs used in the present work contain isooctane (C_8H_{18}) and tetramethylsilane ($Si(CH_3)_4$), respectively, as the sensitive media.

A LIC technology intended for radiation dosimetry in photon and electron beams was first proposed by Wickman (1974). Despite being available for a long time, this technology has not been adopted in clinical radiation dosimetry since the conception. This is due to issues with the performance of LICs, which include several chamber and liquid specific parameters. The main parameters affecting the measurement signal from a LIC are ion recombination effects, radiation quality and temperature dependence, and leakage currents. Despite these issues, several prototypes and commercial products have been introduced since LICs were first proposed, e.g. Wickman *et al* (1998), Eberle *et al* (2003), Pardo *et al* (2005), Stewart *et al* (2007), González-Castaño *et al* (2011), Brualla-González *et al* (2012), and PTW Radiation detector catalogue 2013 (Freiburg, Germany). In the following subsections, a general overview of the issues related to the performance of LICs is given.

2.1. Dielectric liquids

A dielectric media is characterized by that charged particles are strongly bound to the molecules, and the intrinsic conductivity is thus small or negligible, i.e. these media are electric insulators. The electrostatic properties of the nonpolar dielectric liquids employed as the sensitive media in LICs in the present work are given by the dielectric constant (ε_r), also referred to as the relative permittivity. The absolute permittivity, defined as $\varepsilon = \varepsilon_r\,\varepsilon_0$, where ε_0 is the permittivity of free space, describes how an applied electric field affects, and is affected by a dielectric medium. This is thus a central parameter for LICs, where an electric field is applied over the measurement volume containing a liquid to collect the charge created by

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ionization. The value of the dielectric constant used to describe the liquids in the present work is 1.94 and 1.84 for isooctane and tetramethylsilane, respectively (Johansson and Wickman, 1997).

When a liquid contained in plane parallel LIC is irradiated, the created ions will migrate towards the respective electrodes with an average velocity $k_i E$, where k_i is the mobility of an ion species, and E the collecting electric field strength. Values for the positive (k_1) and negative (k_2) ion mobilities for isooctane and tetramethylsilane employed in the present work are those reported by Johansson and Wickman (1997), as shown in table 2.1.1.

Table 2.1.1. Experimentally determined mobilities for positive (k_1) and negative (k_2) ions for isooctane and tetramethylsilane according to the work by Johansson and Wickman (1997).

Liquid	k_1 $\left(\text{m}^2 \text{ s}^{-1} \text{ V}^{-1}\right)$	k_2 $\left(\text{m}^2 \text{ s}^{-1} \text{ V}^{-1}\right)$
Isooctane	$2.9 \cdot 10^{-8}$	$2.9 \cdot 10^{-8}$
Tetramethylsilane	$5.3 \cdot 10^{-8}$	$9.0 \cdot 10^{-8}$

The investigation by Johansson and Wickman (1997) is not the only work on the property of ion mobilities in liquids. This reference was chosen for the convenience of using the same source of experimentally determined ion mobilities for both isooctane and tetramethylsilane. In a recent work, Pardo *et al* (2012) has given a report on experimentally determined ion mobilities for ionized isooctane, where three different species of ions were identified.

Another important parameter for dielectric liquids employed in LICs is the general recombination rate constant (α). Employing the results from the work by Debye (1942), and the ion mobilities reported by Johansson and Wickman (1997), the numerical value of the general recombination rate constant can be determined to $5.4 \cdot 10^{-16}$ and $1.4 \cdot 10^{-15}$ m^{3}s^{-1} for isooctane and tetramethylsilane, respectively. The corresponding values of the general recombination rate constant and the ion mobilities for air are $\alpha = 1.54 \cdot 10^{-12}$ m^3 s^{-1}, $k_1 = 2.10 \cdot 10^{-4}$ m^2 s^{-1} V^{-1}, and $k_2 = 1.36 \cdot 10^{-4}$ m^2 s^{-1} V^{-1} (Boag, 1963). The transport of charge in air-filled ionization chambers is obviously much faster than that in liquids. This will contribute to the comparatively severe general recombination losses in LICs, since low ion mobilities yields a high probability for general recombination.

A complication in the interpretation of experimentally determined ion mobilities for ionized liquids is the presence of impurities. While LICs are manufactured with high purity liquids, it cannot be ruled out that some small amounts of impurities are introduced in the sensitive media during the filling process. Furthermore, impurities may also be introduced into the liquid from the chamber body materials and the electrodes. This has been

discussed in the early experimental works on ionized liquids, e.g. Adamczewski (1965), Hummel and Allen (1966), Schmidt and Allen (1970), as well as in the review of LICs operated at room temperature by Engler (1996). Such impurities, e.g. carbon- or oxygen-based molecules can be effective electron scavengers, introducing an uncertainty in what kind of ion species are transporting the charge in an ionized liquid. The amount and type of impurities will also affect the recombination properties of a liquid employed as the sensitive media in a given LIC, since ion recombination depends on characteristics of the charge carriers created.

2.2. Ion recombination

Ion recombination means that the density of ions created in the sensitive media in an ionization chamber is diminished through charge reduction processes. These processes may lead back to the initial state of neutral molecules, thereby degrading the measurement signal.

In the field of radiation dosimetry, ion recombination is commonly viewed as two separate processes, i.e. initial and general recombination. Initial recombination is considered as the interactions taking place between charges produced in the same incident ionizing particle track. General recombination is the process of neutralization of charge produced in different ionizing particle tracks. This process occurs during the charge migration to the respective electrodes under the influence of the collecting electric field given by the applied voltage to an ionization chamber.

There are several works on the property of describing initial recombination, e.g. Jaffé (1913), Onsager (1938) and Kramers (1952). The works by Jaffé and Kramers are focused on interaction between charges created by densely ionizing radiation, and as such not applicable to radiation dosimetry for photon and electron beams. The Onsager theory, which was derived for sparsely ionizing radiation, is thus more immediately relevant in the present work. Furthermore, the Onsager theory is also interesting to consider for ionized liquids since it was derived from the laws Brownian motion, which is suitable for media such as gases at high pressures. As shown by Debye (1942), liquids and gases at high pressures share common traits.

General recombination in air-filled ionization chambers employed for measurements in continuous beams can be considered as well described in the literature. Here, the Thomson equations (1899) derived to describe the conduction of electricity through an ionized gas are the fundament for the expressions for the general collection efficiency by Seemann (1912) and

Greening (1964). The theoretical background for the general collection efficiency for pulsed beams is not as robust, due to the semi-empirical nature of the work by Boag (1950).

There is presently no dedicated theory for ion recombination in liquids, and the present work thus employs theories derived for gases in an approximate manner to investigate and interpret these processes in liquids. The theories used in the present work, for both initial and general recombination, are described in detail in section 4.

2.3. Radiation quality dependence

The absorbed radiation dose in the sensitive media in an irradiated ionization chamber measurement volume depends on the radiation quality and intensity, as well as the properties of the media. As a consequence, if the ultimate goal of measurements with an ionization chamber is the determination of absorbed dose to a media other than that enclosed in an ionization chamber, cavity theory involving mass-energy absorption ratios and stopping power ratios is commonly employed (TRS-398, IAEA 2000). The reference media, to which the absorbed dose is commonly determined, in radiation dosimetry is water due to the inherent similarities to the energy absorption characteristics of human soft tissue.

The energy absorption properties of liquids employed in LICs are closer to those of water compared to air, leading to smaller displacement and perturbation effects in LICs compared to air-filled ionization chambers, as discussed by Wickman and Nyström (1992). Nevertheless, a treatment similar to that for air-filled ionization chambers employing cavity theory is needed to translate LIC readings by a calibration factor to the corresponding absorbed dose to water. Furthermore, due to the presence of initial recombination in ionized liquids, the energy dependence of LICs is not as straightforward as that for conventional air-filled ionization chambers. As previously discussed, initial recombination is a process between charges originating from the same ionizing particle track, and thus the intra-track ionization density will influence the escape probability from initial recombination. The intra-track ionization density depends on the radiation quality, and the process of initial recombination thus implicitly depends on the radiation quality. The escape probability from initial recombination decreases with increasing intra-track ionization density, which leads to a decrease in the measurement signal from a LIC for a given collecting electric field strength (Schmidt, 1997).

2.4. Temperature dependence

Similarly to the case of air-filled ionization chambers, the measurement signal from a LIC is dependent on the temperature of the sensitive media. However, contrary to the behaviour of air-filled ionization chambers, the measurement signal from a LIC has been observed to increase with an increased temperature (Wickman and Nyström 1992, Wickman *et al* 1998). For sparsely ionizing radiation, this behaviour of ionized liquids has been explained by application of the Onsager theory for initial recombination (1938) to experimental data from ionized liquids by Schmidt and Allen (1970). A custom-built LIC has also been investigated by employing the Onsager theory, where the results by Schmidt and Allen have been confirmed for isooctane (Franco *et al*, 2006). The temperature dependence of the escape probability from initial recombination according to the Onsager theory is detailed in section 4.1.

Where applicable, the LIC readings in the present work have been corrected for their respective temperature dependencies depending on the liquid employed as the sensitive media (isooctane and tetramethylsilane), according to the work by Wickman *et al* (1998).

2.5. Leakage currents

Leakage currents yield a measurement signal from an ionization chamber in the absence of an applied ionizing agent. The magnitude of the leakage current in an ionization chamber for a given applied voltage is an important parameter, since this will set a lower limit for the practically applicable range of dose rates.

Theoretically, applying an electric field over an ideal dielectric liquid free from impurities cannot yield leakage currents since the electronic conduction levels are well separated by forbidden gaps, and thus thermal excitation of charge carriers can be neglected (Engler, 1996). However, in a realistic situation the presence of impurities, such as molecules or atoms with low ionization potentials and polar molecules, can result in a non-negligible intrinsic conductivity and thus also leakage currents in the media (Schmidt, 1997).

Efficient insulators separating the electrodes and guard rings are commonly employed in ionization chamber design, which have a damping effect on the magnitude of leakage currents. For the PTW microLion LICs used in the present work, the electrodes are separated by Rexolite ®, which is a highly

efficient and radiation resistant insulator, outside the cylindrical measurement volume containing the liquid. However, the microLion LIC does not have a guard ring, which may increase the leakage current.

The leakage currents in the microLion LICs containing isooctane and tetramethylsilane, respectively, recorded in the experiments in the present work are in the 10^{-15} A range. All LIC readings in the experiments performed in the present work have been corrected for leakage currents.
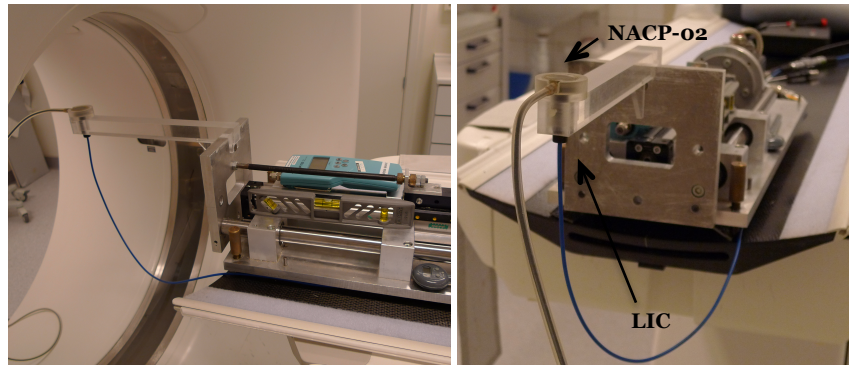
3. Experiments

The experimental part of the investigation of general recombination in liquids in the present work is based on measurements performed in continuous beams of 120 kV x-rays (paper I) and 511 keV annihilation photons (paper II), as well as pulsed beams of 20 MeV electrons (Tölli *et al*, 2010).

Two microLion LICs (PTW, Germany) containing isooctane and tetramethylsilane, respectively, have been used in all experiments in the present work. Furthermore, plane parallel air-filled NACP-02 chambers have been employed as a reference to monitor the radiation output, as well as to supply the reference signal used in the two-dose-rate method for both continuous and pulsed beams.

3.1. Continuous beams - 120 kV x-rays

The experiments in paper I were performed in continuous beams of 120 kV x-rays from a computed tomography unit (GE LightSpeed VCT) in the Department of Radiology at Norrlands University Hospital (Umeå, Sweden). The LICs and the monitor NACP-02 chamber were arranged in the beam path by a custom-built holder to allow for reproducible measurements. The computed tomography unit was operated without a bow tie filter in the beam path and the nominal collimation of the x-ray beam in the z-axis was set to 40 mm. The experimental setup is shown in figure 3.1.1.

Figure 3.1.1. The experimental setup for the experiments involving 120 kV x-rays. Shown here is the LIC and NACP-02 chamber arrangement in the custom-built holder placed on the computed tomography unit patient couch.

Six different x-ray tube currents were employed in the experiments, and the corresponding dose rates in the measurement geometry were estimated by

measurements with a Farmer chamber of type 2505/3A (Nuclear Enterprises Ltd.) calibrated for air kerma. The x-ray quality calibration of the Farmer chamber was performed at the Swedish Radiation Safety Authority secondary standard dosimetry laboratory (SSDL). A summary of the computed tomography unit settings, and the corresponding dose rates estimated by measurements with the Farmer chamber is shown in table 3.1.1.

Table 3.1.1. Computed tomography unit settings and the corresponding dose rates in the measurement geometry estimated by a Farmer chamber type 2505/3A (Nuclear Enterprises Ltd.) calibrated for air kerma in x-ray radiation qualities.

Parameter	Sequence					
	I	II	III	IV	V	VI
Tube voltage (kV)	120	120	120	120	120	120
Tube current (mA)	50	100	150	200	250	300
Dose rate (Gy min^{-1})	2.2	4.4	6.5	8.7	10.9	13.0

The charge from all ionization chambers used in the experiments was collected by UNIDOS electrometers (PTW, Germany), one of which also supplied the high voltage to the NACP-02 chamber. A Keithley model 248 High Voltage Unit supplied the voltages to the LICs (100 – 900 V), corresponding to average collecting electric field strengths between 0.3 and 2.6 MV m^{-1}.

The NACP-02 and Farmer chamber readings were corrected for their respective temperature and pressure dependencies by conventional methods (TRS-398, IAEA 2000). Furthermore, the readings from these air-filled ionization chambers were corrected for their respective general recombination losses according to the two-voltage method (TRS-398, IAEA 2000).

3.2. Continuous beams - 511 keV annihilation photons

The experiments in paper II employed the radiation chemistry facilities at Norrlands University Hospital (Umeå, Sweden) to perform measurements in continuous beams of 511 keV annihilation photons resulting from the decay of the radioactive isotope Fluorine-18 (^{18}F). The same ionization chambers, both the reference chamber and the LICs, as in the experiments involving 120 kV x-rays were used for these measurements. An initial activity of approximately 250 GBq ^{18}F was transported to a hot cell, where the decaying activity employed as the radiation source was contained in a glass vial. The glass vial was arranged in a custom-built holder for the reference NACP-02 chamber and the LICs, respectively. Schematic illustrations of the measurement setup for annihilation photons are shown in figure 3.2.1.
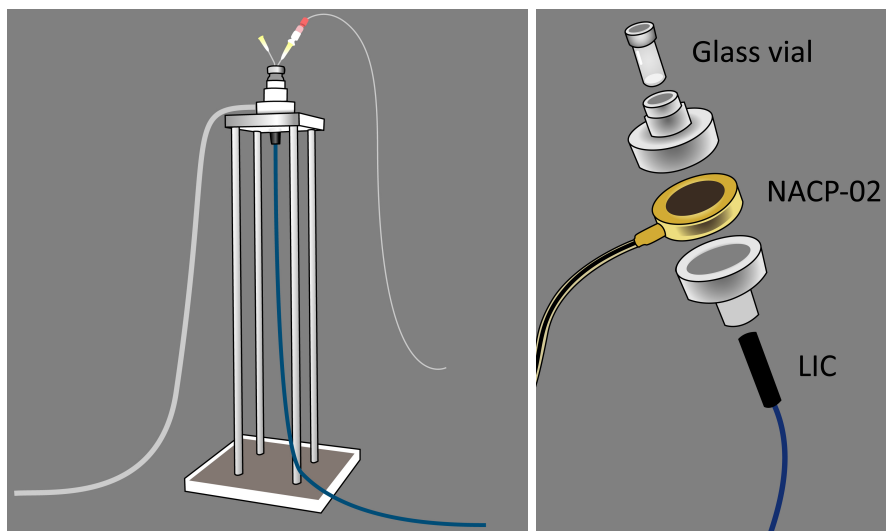
Figure 3.2.1. Schematic illustrations representing the measurement setup for the experiments involving 511 keV annihilation photons. Shown here is the LIC and NACP-02 chamber arrangement in the custom-built holder together with the glass vial containing the radiation source activity of ^{18}F.

The maximum dose rate in which the experiments involving annihilation photons were performed was determined by Monte Carlo simulation to approximately 1.0 Gy min^{-1}. In the determination of the maximum dose rate, MCNPX v. 2.7.c was used together with Visual Editor v. X_24b. Since the primary aim of the present work involves a study of general recombination, a lower regime of applied voltages was used for annihilation photons (25 – 300 V) compared to 120 kV x-rays. These applied voltages correspond to average collecting electric field strengths between 0.07 and 1.4 MV m^{-1}.

Parallel measurements with the LICs containing isooctane and tetramethylsilane, respectively, and the reference NACP-02 chamber were performed during the decay of each batch of ^{18}F, i.e. for each applied voltage to the LICs. The charge readings from the ionization chambers were recorded by a custom LabView program, which allows correlation of the readings from the LICs and the reference chamber by time stamps. Before analysing general recombination for each applied voltage and liquid, perturbations in the measurement signal from the LICs were observed. In the parallel measurements performed with the NACP-02 chamber, no perturbations could be found in the chamber readings. Examples of the perturbations are shown in figure 3.2.2 for the LIC containing isooctane at an applied voltage of 300 V, as well as the corresponding reference signal from the NACP-02 chamber. Also shown in figure 3.2.2 are results from an additional measurement series for the microLion LIC containing isooctane

for an applied voltage of 500 V. This additional measurement series was performed to investigate the perturbations for an applied voltage closer to the manufacturer recommendations (800 V).
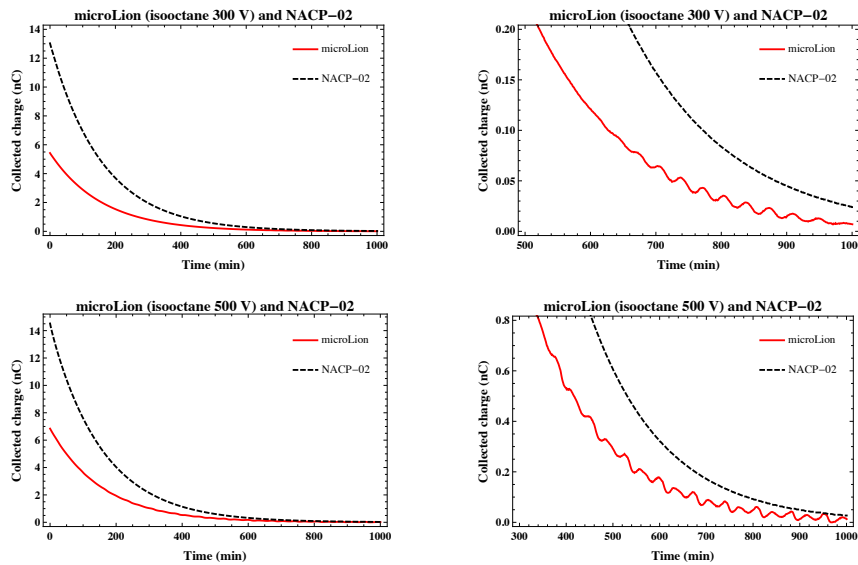
Figure 3.2.2. Examples of the perturbations observed in the LIC readings in the experiments involving 511 keV annihilation photons. Shown here are the readings from the reference NACP-02 chamber and the microLion LIC containing isooctane correlated by time stamps, for applied voltages to the LIC of 300 and 500 V, respectively.

As seen in figure 3.2.2, the perturbations in the LIC readings were observed to increase in strength with an increased applied voltage. When the perturbations in the LIC charge readings were compared to the temperature variations recorded by the clean room monitoring system in the radiation chemistry laboratory a correlation was found, as shown in figure 3.2.3 (upper panels).
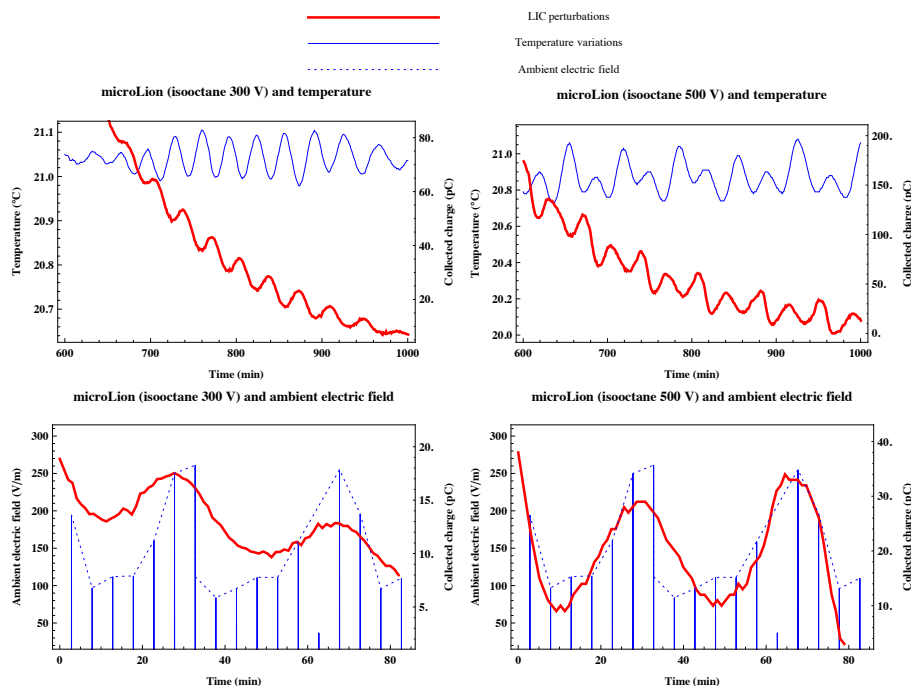
Figure 3.2.3. Temperature variations recorded by the clean room monitoring system and the perturbations in the LIC readings (upper panels) correlated by time stamps. Ambient electric fields measured by an electric field probe manually correlated to the perturbations in the LIC readings (lower panels).

As seen in figure 3.2.3, the temperature variations were small ($< 0.4\,°C$) during the experiments and the LIC reading perturbations displayed a decrease with increasing temperature, which is the opposite of what should be expected (Wickman and Nyström 1992, Wickman *et al* 1998, Franco *et al* 2006). The temperature dependence of isooctane for the present applied voltages reported by Franco *et al* is $0.3 - 0.6\%\,°C^{-1}$, and it was thus ruled out that temperature variation in the liquid sensitive media was the cause of the perturbations of the magnitude observed. An investigation of possible sensitivity in the microLion LIC design to ambient electric fields present in the radiation chemistry facilities was performed with the aid of an electric field probe (C.A 42 EF400, Chauvin Arnoux, France). Measurement results from the probe, in the frequency range 5 Hz to 3.2 kHz, displayed a temporal variation that coincided with the perturbations observed in the LIC charge readings. Examples of measurement results from the electric field probe that correlated to the perturbations observed in the LIC readings are shown in figure 3.2.3 (lower panels). It was thus concluded in paper II that the PTW microLion LIC is sensitive to ambient electric fields. This may compromise the reliability of the microLion LIC, since ambient electric fields of the

strength observed to cause perturbations in paper II can be found in many common situations.

3.3. Pulsed beams - 20 MeV electrons

In the comparative investigation of the performance of the two-dose-rate and three-voltage methods in paper III, experimental data from both continuous and pulsed beams were analysed. For the investigation of the respective methods for the case of pulsed beams, measurement data from the experiments involving pulsed beams of 20 MeV electrons by Tölli *et al* (2010) were employed (personal communication).

In the experiments performed by Tölli *et al* (2010), a MM50 Racetrack Microtron (Scanditronix Medical AB, Sweden) accelerator was employed to supply 20 MeV electron beams with a dose per pulse between 0.1 and 8 mGy pulse^{-1}. The pulse rate of the beam was set to 50 Hz to avoid pulse overlapping in the signal from the LICs due to low ion mobilities. The field size in the isocentre of the water phantom used in the measurements was 10 x 10 cm^2. For the investigation of general recombination, the LICs were operated at applied voltages between 300 and 900 V, and a cross-calibrated NACP-02 reference chamber was employed to estimate the dose per pulse in the electron beam. Peripheral measurement equipment employed for the experiments involving pulsed beams, such as high voltage supplies and electrometers were the same as those used in paper I.

4. Theory for ion recombination

There are presently no dedicated theories for ion recombination in liquids, neither for initial nor general recombination. The present work is thus based on the approach of employing theories derived for gases by approximation for LICs. Theory for general recombination in gases (Seemann 1912, Boag 1950, Greening 1964) has been used with promising results for applications with LICs for both continuous (Wickman and Johansson, 1997) and pulsed beams (Johansson *et al*, 1997). Furthermore, the Onsager theory for initial recombination (1938) has also been applied to LICs containing isooctane with encouraging results (Pardo *et al*, 2004).

In the following subsections, detailed accounts of theories for initial and general recombination in gases employed for the study of LICs in the present work are given in modern physics notation.

4.1. Initial recombination

Jaffé (1913) derived a theory to describe initial recombination for densely ionizing radiation. This theory is based on the assumption that the electron distributions created by ionization forms a column around the incident ionizing particle track, and that once the electrons have thermalized, diffusion and recombination may take place. According to the theory, the created charge density (n) in each point changes with time due to diffusion and recombination as

$$\frac{\partial n}{\partial t} = D\nabla^2 n - \alpha n^2. \tag{4.1.1}$$

Here, D and α are the diffusion and recombination coefficients, respectively. It was noted by Jaffé, as well as Kramers (1952), that recombination is the dominating process leading to the loss of charge in liquids. By neglecting diffusion it is possible to find a solution to (4.1.1) for liquids, which may be used for the determination of initial recombination losses along the track of a densely ionizing particle.

The present work is focused on less densely ionizing radiation than that considered by Jaffé, i.e. photon and electron beams, and Jaffé's results are thus not intuitively applicable. A further disadvantage with the Jaffé theory is that it lacks an explicit dependence on the Coulomb interaction between positive and negative charges. Since the average thermalization distance in a

liquid is in the nanometre range, Coulomb interaction cannot be assumed to be negligible.

In contrast to the work done by Jaffé, the Onsager theory for initial recombination (1938) for sparsely ionizing radiation includes an explicit dependence on the Coulomb field. Onsager considers a single ion pair created by ionization in a gas under high pressure, where an electron has been liberated from a molecule and is thermalized at some distance from the place of origin. Liberated electrons are divided into two categories, i.e. free or bound. If the thermalization distance fulfils $r_t > r_0$ in the Onsager framework, a liberated electron is considered as free and thus cannot recombine with a parent ion. An electron is considered as bound according to the theory if the thermalization distance (r_t) fulfils the criteria

$$r_t < \frac{r_0}{2} = \frac{1}{2} \frac{e^2}{4\pi\varepsilon k_B T}. \tag{4.1.2}$$

Here, $\varepsilon = \varepsilon_0 \varepsilon_r$, where ε_0 and ε_r represent the permittivity of free space and the relative permittivity of the ionized media, respectively, k_B the Boltzmann constant, T the absolute temperature, e the elementary charge, and r_0 the Onsager radius, which represents the distance between a liberated electron and a parent ion where the Coulomb energy equals the thermal energy ($k_B T$). If the thermalization distance fulfils (4.1.2), the fate of a liberated electron is determined by the combined action of thermal motion, the attraction of the Coulomb potential, as well as the action of an external applied electric field. Furthermore, under steady state conditions, Onsager solved the equation of Brownian motion

$$\nabla \cdot \left[\left(e^{-\phi(r,\theta)/k_B T} \right) \nabla P(r,\theta) \right] = 0, \tag{4.1.3}$$

which can be employed to determine the fraction of initially bound electrons that escape initial recombination with a parent ion $\left(P(r,\theta) \right)$. In (4.1.3), the potential energy $\left(\phi(r,\theta) \right)$ is given by

$$\phi(r,\theta) = -e\,E\,\cos(\theta) - \frac{1}{4\pi\varepsilon} \frac{e^2}{r}, \tag{4.1.4}$$

where r represents the initial separation between a liberated electron and a parent ion, E the external applied electric field acting upon the electron-ion pair, and θ the angle between the external applied electric field lines and the vector from the parent molecule to the liberated electron.

According to the Onsager theory, initial recombination takes place between a liberated electron and a parent ion, and no other charges may interfere with

this interaction. This theory should therefore be most well adapted to very sparsely ionizing radiation, due to the requirement on the charge density created in each ionizing particle track. However, the Onsager theory has been experimentally investigated for liquids in clinically realistic radiation qualities with quite good predictions of initial recombination losses (Pardo *et al*, 2004). For isooctane and tetramethylsilane employed as the liquid sensitive media in the present work, the Onsager distance is 29 and 31 nm at 20 °C, respectively. This can be compared to the average thermalization distance, which is also in the nanometre range, e.g. 17 nm for tetramethylsilane as measured by Engler *et al* (1993). Furthermore, in a compilation of experimental data found in the literature for nonpolar dielectric liquids, Jay-Gerin *et al* (1993) have reported average thermalization distances of 11 and 16 nm, respectively, for isooctane and tetramethylsilane. The Onsager theory applied to liquids thus predicts extensive initial recombination in ionized isooctane and tetramethylsilane.

A complication with the Onsager theory applied to media ionized by photon and electron beams is that some of the ions created may be multiply charged, which will affect the Onsager distance, i.e. increasing the probability of initial recombination. Here, the Coulomb field from charges created in the vicinity of the electron-ion pair considered may perturb the Coulomb potential. However, in sparsely ionizing radiation beams the average distance between successive electron-ion pairs can be expected to be quite large, and Coulomb field perturbations may therefore be considered as negligible. The Onsager theory is thus applicable for a situation where the distance between electron-ion pairs created by ionization is large compared to the average electron thermalization distance, and where the created ions are predominantly singly charged.

Onsager solved (4.1.3), and could thus express the escape probability from initial recombination $\big(P(r,\theta)\big)$ as

$$P(r,\theta) = \mathrm{e}^{-\beta\, r\,(1+\cos(\theta))} \int_{r_0/r}^{\infty} J_0\big(2(-\beta\, r\,(1+\cos(\theta))\, s)^{1/2}\big)\, \mathrm{e}^{-s} ds, \qquad (4.1.5)$$

where J_0 is the zero-order Bessel function, $\beta = e\, E/(2\, k_B\, T)$, and the other parameters have their previous meanings.

The results from Onsager were later employed in the work by Mozumder (1974a), where (4.1.5) was reformulated using a single series expansion and by averaging over all angles (θ). The work by Mozumder gives a relation for the escape probability from initial recombination $\big(P(r,E,T)\big)$ as a function of

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the initial separation (r), collecting electric field strength (E) and absolute temperature (T) as

$$P(r, E, T) = 1 - \frac{E_0\, r_0}{2\, E\, r} \sum_{k=0}^{\infty} A_k \left(\frac{r_0}{r}\right) A_k \left(\frac{2\, E\, r}{E_0\, r_0}\right), \tag{4.1.6}$$

where

$$A_k(\eta) = \mathrm{e}^{-\eta} \sum_{n=2k+1}^{\infty} \frac{\eta^{n-k}}{(n-k)!} = \mathrm{e}^{-\eta} \sum_{m=k+1}^{\infty} \frac{\eta^m}{m!} =$$

$$= 1 - \mathrm{e}^{-\eta} \left(1 + \eta + \frac{\eta^2}{2!} + \cdots + \frac{\eta^k}{k!}\right), \tag{4.1.7}$$

$$E_0 = \frac{2\, k_B\, T}{e\, r_0} = \left\{r_0 = \frac{e^2}{4\,\pi\,\varepsilon\, k_B\, T}\right\} = \frac{8\,\pi\,\varepsilon\,(k_B\, T)^2}{e^3}. \tag{4.1.8}$$

Here, the parameter E_0 (4.1.8) is commonly referred to as the Onsager field. Furthermore, Mozumder employed a power series expansion of the collecting electric field strength (E) in (4.1.6). This allows for a more convenient representation of the escape probability from initial recombination, e.g. as given by Pardo *et al* (2004), as

$$P(r, E, T) = \mathrm{e}^{-r_0/r} \left(1 + \sum_{n=1}^{\infty} \left(\frac{E}{E_0}\right)^n B_n \left(\frac{r}{r_0}\right)\right), \tag{4.1.9}$$

where

$$B_n \left(\frac{r}{r_0}\right) = \sum_{m=1}^{n} \left(\left(\sum_{k=m}^{n} F_k^n\right) \frac{(r/r_0)^{(n-m)}}{m!}\right). \tag{4.1.10}$$

The numerical coefficients F_k^n in (4.1.10) were detailed in the work by Mozumder. Given a description of the distribution of electron thermalization distances $\left(F(r)\right)$ that can be convoluted with (4.1.9), the escape probability from initial recombination as a function of experimental conditions, i.e. the collecting electric field strength (E) and absolute temperature (T), can be expressed as

$$P(E, T) = \int_0^{\infty} F(r)\, P(r, E, T)\, dr. \tag{4.1.11}$$

Several authors have investigated suitable expressions for the distribution function of thermalization distances $\left(F(r)\right)$, including delta functions, Gaussian type functions, as well as exponential functions (Mozumder 1974b, Muñoz and Drijard 1992, Pardo *et al* 2004).

For low collecting electric field strengths, the series expansion in (4.1.9) is well approximated by the term corresponding to $n = 1$. This approximation can, by employing the definition of the Onsager field (4.1.8) be expressed as

$$P(r, E, T) = e^{-r_0/r} \left(1 + \frac{E}{E_0} + \cdots \right). \tag{4.1.12}$$

A commonly used quantity related to initial recombination is the free-ion yield (G_{fi}), which is defined as the amount of electron-ion pairs escaping initial recombination per 100 eV deposited energy in an ionized media. Integrating the escape probability from initial recombination (4.1.12) over all possible thermalization distances, the free-ion yield can according to Mozumder's treatment of the Onsager theory be expressed as

$$G_{fi}(E, T) = N_0 \, P(E, T) = G_{fi}^0 \left(1 + \frac{E}{E_0} + \cdots \right). \tag{4.1.13}$$

Here, N_0 represents the total amount of electron-ion pairs created per 100 eV deposited energy, and G_{fi}^0 the free-ion yield in the absence of an external applied electric field. Relation (4.1.13) is the form of the Onsager theory employed to model initial recombination in the three-voltage method (Pardo-Montero and Gómez, 2009) for general recombination correction for LICs that was investigated in paper III.

4.2. General recombination in continuous beams

Thomson (1899) proposed the use of four equations for describing the transport of charge in a continuously irradiated plane parallel gas-filled ionization chamber. These equations are given by

$$\frac{dE}{dx} = \frac{e}{\varepsilon}(n_1 - n_2),$$
(4.2.1)

$$\frac{d}{dx}(k_1\, n_1\, E) = n_0 - \alpha\, n_1\, n_2,$$
(4.2.2)

$$-\frac{d}{dx}(k_2\, n_2\, E) = n_0 - \alpha\, n_1\, n_2,$$
(4.2.3)

$$J = e\, k_1\, n_1\, E + e\, k_2\, n_2\, E.$$
(4.2.4)

Here, E represents the collecting electric field strength between the electrodes, x the distance from the geometric centre of the measurement volume, n_1 and n_2 the respective densities of positive and negative ions created, k_1 and k_2 the corresponding ion mobilities, n_0 the amount of ions created per unit time and volume, α the general recombination rate constant, e the elementary charge, $\varepsilon = \varepsilon_0\, \varepsilon_r$, where ε_0 and ε_r represent the permittivity of free space and the relative permittivity of the ionized media, respectively, and J the current density created by ionization. The spatial dependence of the collecting electric field $(E(x))$, and the respective densities of positive and negative ions $(n_1(x), n_2(x))$, have been left out of the Thomson equations here for a notation that is easier to manage in further derivations.

The Thomson equations describe how the collecting electric field is influenced by the charge densities of positive and negative ions created by continuous ionization, by the differential form of Gauss theorem (4.2.1). Furthermore, the equations describe the dose rate dependent ion recombination per unit time and volume (4.2.2, 4.2.3) given a continuous and constant ionization, i.e. according to the continuity equation for positive and negative ions, respectively. Here, the relationship between ion recombination and the charge densities with corresponding ion mobilities is defined, e.g. a high charge density and low ion mobility will result in a large amount of ion recombination. Finally, the equations relate the current density to the collecting electric field strength through the charge densities created and the respective ion mobilities (4.2.4).

Given that the ion mobilities are constant everywhere in the collecting electric field, we can reformulate (4.2.2) and (4.2.3) and take the sum of the respective expressions as

$$\frac{d}{dx}(n_1 E) - \frac{d}{dx}(n_2 E) = (n_0 - \alpha\, n_1\, n_2)\left(\frac{1}{k_1} + \frac{1}{k_2}\right). \qquad (4.2.5)$$

Furthermore, from relation (4.2.1) we may reformulate n_1 as

$$n_1 = \frac{\varepsilon}{e}\frac{dE}{dx} + n_2. \qquad (4.2.6)$$

Employing (4.2.6) with (4.2.5) yields

$$\frac{d}{dx}\left(E\left(\frac{\varepsilon}{e}\frac{dE}{dx} + n_2\right)\right) - \frac{d}{dx}(n_2 E) = \frac{\varepsilon}{e}\frac{d}{dx}\left(E\frac{dE}{dx}\right) =$$

$$= (n_0 - \alpha\, n_1\, n_2)\left(\frac{1}{k_1} + \frac{1}{k_2}\right), \qquad (4.2.7)$$

and since $\frac{d}{dx}\left(E\frac{dE}{dx}\right) = \frac{1}{2}\frac{d^2E^2}{dx^2}$, we have

$$\frac{d^2E^2}{dx^2} = \frac{2\,e}{\varepsilon}(n_0 - \alpha\, n_1\, n_2)\left(\frac{1}{k_1} + \frac{1}{k_2}\right). \qquad (4.2.8)$$

By combining (4.2.1) and (4.2.4), the respective charge densities of positive and negative ions may be expressed as

$$n_1 = \frac{1}{e\,E\,(k_1+k_2)}\left(J + k_2\,\varepsilon\,\frac{dE^2}{dx}\right), \qquad (4.2.9)$$

$$n_2 = \frac{1}{e\,E\,(k_1+k_2)}\left(J - k_1\,\varepsilon\,\frac{dE^2}{dx}\right). \qquad (4.2.10)$$

Inserting (4.2.9) and (4.2.10) in (4.2.8) we can formulate a differential equation for the collecting electric field in a continuously irradiated plane parallel gas-filled ionization chamber

$$\frac{d^2E^2}{dx^2} = \frac{2\,e}{\varepsilon}\left(\frac{1}{k_1} + \frac{1}{k_2}\right)\cdot$$

$$\cdot\left(n_0 - \frac{\alpha}{e^2\,E^2\,(k_1+k_2)^2}\left(J + k_2\,\varepsilon\,\frac{dE^2}{dx}\right)\left(J - k_1\,\varepsilon\,\frac{dE^2}{dx}\right)\right). \qquad (4.2.11)$$

Thomson was not able to solve the differential equation (4.2.11) in closed form, except for the case $k_1 = k_2$ and very small current densities, as detailed in the work by Thomson and Thomson (1928).

Mie (1904) used the Thomson equations to derive a differential equation akin to (4.2.11), aiming to describe the relative collecting electric field

strength $\left(\sqrt{z}\right)$ for a continuously irradiated plane parallel gas-filled ionization chamber. The resulting differential equation is given by

$$\frac{1-\mu^2}{2\,\lambda}\,z\,\frac{d^2z}{d\zeta^2} - \frac{1-\mu^2}{4\,\lambda^2}\left(\frac{dz}{d\zeta}\right)^2 + \frac{\mu}{\lambda}\frac{dz}{d\zeta} - z + 1 = 0, \tag{4.2.12}$$

where

$$z = \left(\frac{E}{a}\right)^2, \tag{4.2.13}$$

$$a^2 = \frac{J^2}{n_0}\frac{\alpha}{e^2\,(k_1+k_2)^2}, \tag{4.2.14}$$

$$\mu = \frac{k_1-k_2}{k_1+k_2}, \tag{4.2.15}$$

$$\lambda = \frac{e\,(k_1+k_2)}{\alpha\,\varepsilon}, \tag{4.2.16}$$

$$\zeta = \frac{J_M}{J}\frac{x}{(h/2)}. \tag{4.2.17}$$

Here, h is the electrode separation and J_M the amount of charge created per unit time and area that corresponds to a theoretical maximum current, i.e. corresponding to no general recombination losses. As discussed in paper IV, in the formulation of the relative collecting electric field strength $\left(\sqrt{z}\right)$, Mie employed an approximation of the resistivity (ρ) of the ionized media

$$\rho = R\frac{A_e}{h} = \frac{E}{J} = \frac{1}{e\,(k_1+k_2)\,\sqrt{\frac{n_0}{\alpha}}}, \tag{4.2.18}$$

where A_e is the electrode area and R the resistance of the ionized media. The resistivity of the ionized media is thus defined by material specific constants, i.e. the ion mobilities (k_1, k_2) and the general recombination rate constant (α), as well as the intensity of the continuous radiation beam, i.e. the amount of ions created per unit time and volume (n_0). The approximation in (4.2.18) was derived by considering that the resistivity is specific for the ionized media and the case of $\frac{dz}{d\zeta} = 0$, which Mie deduced to mean that $z = 1$. Furthermore, Mie solved the differential equation (4.2.12) by series expansion for two cases, i.e. weak and strong ionization currents, where the latter case represents currents greater than $0.57 \cdot J_M$ for air-filled ionization chambers. The solution for strong currents, which was employed to derive the oft cited general collection efficiency according to Mie (Seemann, 1912), is given by

$$\sqrt{z} = \sqrt{\frac{2}{3\,(1-\mu^2)\,(1-\varrho)\,\varrho}} \left(1 + \varrho \left(-\frac{3\,\lambda+8}{20} + \frac{3\,\lambda\,\mu}{2}\,\frac{x}{(h/2)} + \frac{3\,\lambda}{4}\left(\frac{x}{(h/2)}\right)^2\right)\right), \qquad (4.2.19)$$

where

$$\varrho = \frac{J_M - J}{J_M}. \qquad (4.2.20)$$

These relations thus describe the distortion of the relative collecting electric field between the electrodes, following the densities of positive and negative charge created by ionization through the parameter ϱ, i.e. the space charge effect.

The space charge effect for a continuously irradiated NACP-02 plane parallel air-filled ionization chamber according to the work by Mie for strong currents (4.2.19) is shown in figure 4.2.1. Here, general collection efficiencies of 0.95, 0.99 and 0.999, respectively, have been used in the calculations.
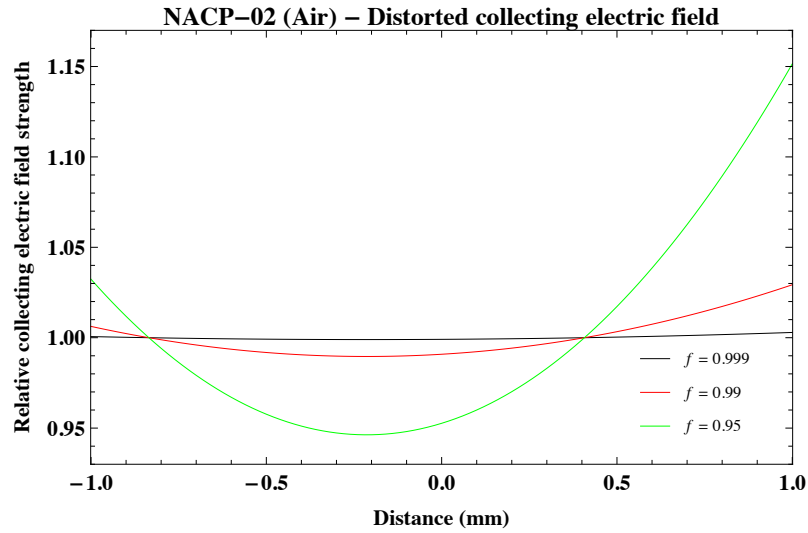
Figure 4.2.1. The space charge effect, as given by the results from the work by Mie (1904) for a NACP-02 air-filled plane parallel ionization chamber. Numerical values for the respective ion mobilities and the general recombination rate constant for air have been taken from the work by Boag (1963).

In the calculations of the distorted collecting electric fields shown in figure 4.2.1, the work by Boag (1963) was consulted for values for the ion mobilities and the general recombination rate constant. Furthermore, $\lambda = 3.56$ has been employed to represent air (Mie, 1904), and the electrode separation for the NACP-02 chamber used was $h = 2$ mm. As seen in figure 4.2.1, the work by Mie predicts that the distortion of the collecting electric field increases as

the general collection efficiency decreases, i.e. the space charge effect increases with increasing dose rate.

From (4.2.19) and (4.2.20) the potential difference (U) between the electrodes can be related to the resistance of the ionized media and the current density as

$$U = \int_{-h/2}^{h/2} E \, dx = \frac{A_e \, R \, J}{h} \int_{-h/2}^{h/2} \sqrt{z} \, dx =$$

$$= A_e \, R \, \sqrt{\frac{2}{3 \, (1-\mu^2)}} \sqrt{\frac{J_M \, J}{1-J/J_M}} \left(1 - \frac{4-\lambda}{10} \left(1 - \frac{J}{J_M} \right) \right). \tag{4.2.21}$$

The general collection efficiency (f) of an ionization chamber can be derived from (4.2.21) by the following argument

$$f = \frac{J}{J_M}, \tag{4.2.22}$$

$$\left(\frac{U/A_e}{J_M \, R} \right)^2 = \frac{2}{3 \, (1-\mu^2)} \frac{f}{1-f} \left(1 - \frac{4-\lambda}{10} (1-f) \right)^2. \tag{4.2.23}$$

Furthermore, the resistance of the ionized media, according to the approximation made by Mie (4.2.18), and J_M can be expressed as

$$R = \rho \frac{h}{A_e} = \frac{1}{e \, (k_1+k_2) \sqrt{\frac{n_0}{\alpha}}} \frac{h}{A_e}, \tag{4.2.24}$$

$$J_M = q_0 \, h, \tag{4.2.25}$$

where $q_0 = e \, n_0$ represents the amount of charge created per unit time and volume. By combining (4.2.24) and (4.2.25) we get

$$(J_M \, R)^2 = \frac{1}{A_e^2} \frac{q_0 \, \alpha \, h^4}{(k_1+k_2)^2 \, e}. \tag{4.2.26}$$

Finally, (4.2.23) and (4.2.26) can be used to formulate the general collection efficiency in accordance with the expression proposed by Seemann (1912) as

$$f = \frac{1}{1 + \frac{1}{6} \xi^2 \left(1 - \frac{4-\lambda}{10} (1-f) \right)^2}, \tag{4.2.27}$$

where

$$\xi^2 = m^2 \frac{q_0\, h^4}{U^2}, \text{ and } m = \left(\frac{\alpha}{e\, k_1\, k_2}\right)^{1/2}. \tag{4.2.28}$$

Armstrong and Tate (1964) solved the Thomson equations by numerical methods and compared the results to the general collection efficiency according to Seemann for an air-filled plane parallel ionization chamber. The agreement between the numerical solution and the expression given by Seemann was good for both equal and unequal ion mobilities for general collection efficiencies above 70%.

Greening (1964) adopted an approximation of the general collection efficiency first suggested by Seemann, in which air is specifically considered as the ionized media

$$f = \frac{1}{1 + \frac{1}{6}\xi^2}. \tag{4.2.29}$$

This approximation was done by employing $\lambda = 3.56$ for air (Mie, 1904), and considering the numerical value of the parenthesis in the denominator of (4.2.27) for general collection efficiencies above 70%. There was a minor error in the formulation made by Greening, which was pointed out and corrected by Katoh (1965). The general collection efficiency according to Greening has been employed in the two-dose-rate method for continuous beams in paper I and II.

A better approximation of the general collection efficiency according to Seemann than that proposed by Greening can be achieved, as shown in paper IV. This approximation is derived by first considering the parenthesis in the denominator of (4.2.27)

$$\left(1 - \frac{4-\lambda}{10}(1-f)\right)^2 = \left(1 - \frac{4-\lambda}{5}(1-f) + \left(\frac{4-\lambda}{10}\right)^2 (1-f)^2\right) \approx$$

$$\approx \left\{\left(\frac{4-\lambda}{10}\right)^2 (1-f)^2 \ll 1 - \frac{4-\lambda}{5}(1-f)\right\} \approx \left(1 - \frac{4-\lambda}{5}(1-f)\right). \tag{4.2.30}$$

If the quadratic term is truncated by the approximation stated in (4.2.30), the media specific parameter λ is retained and the resulting general collection efficiency is expressed as a second order polynomial, which has the following solution

$$f = \frac{1}{2} - \frac{15}{\xi^2\,(4-\lambda)} - \frac{5}{2\,(4-\lambda)} \pm \sqrt{\left(\frac{30}{\xi^2\,(4-\lambda)} + \frac{5}{(4-\lambda)} - 1\right)^2 + \frac{120}{\xi^2\,(4-\lambda)}}. \tag{4.2.31}$$

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Considering that the general collection efficiency is positive, the negative root solution in (4.2.31) can be neglected, thus providing an alternative expression for f. This new approximation of the general collection efficiency for continuous beams was employed in the two-dose-rate method for continuous beams in paper IV with a value of λ specific for liquids (Debye, 1942).

The differences between the expressions for the general collection efficiency according to Seemann, Greening and relation (4.2.31) derived in paper IV are shown in figure 4.2.2 for both air and liquid employed as the sensitive media. Here, the value of the parameter λ for air has been taken from Mie, and the work by Debye (1942) has been consulted for the corresponding value for a dielectric liquid.
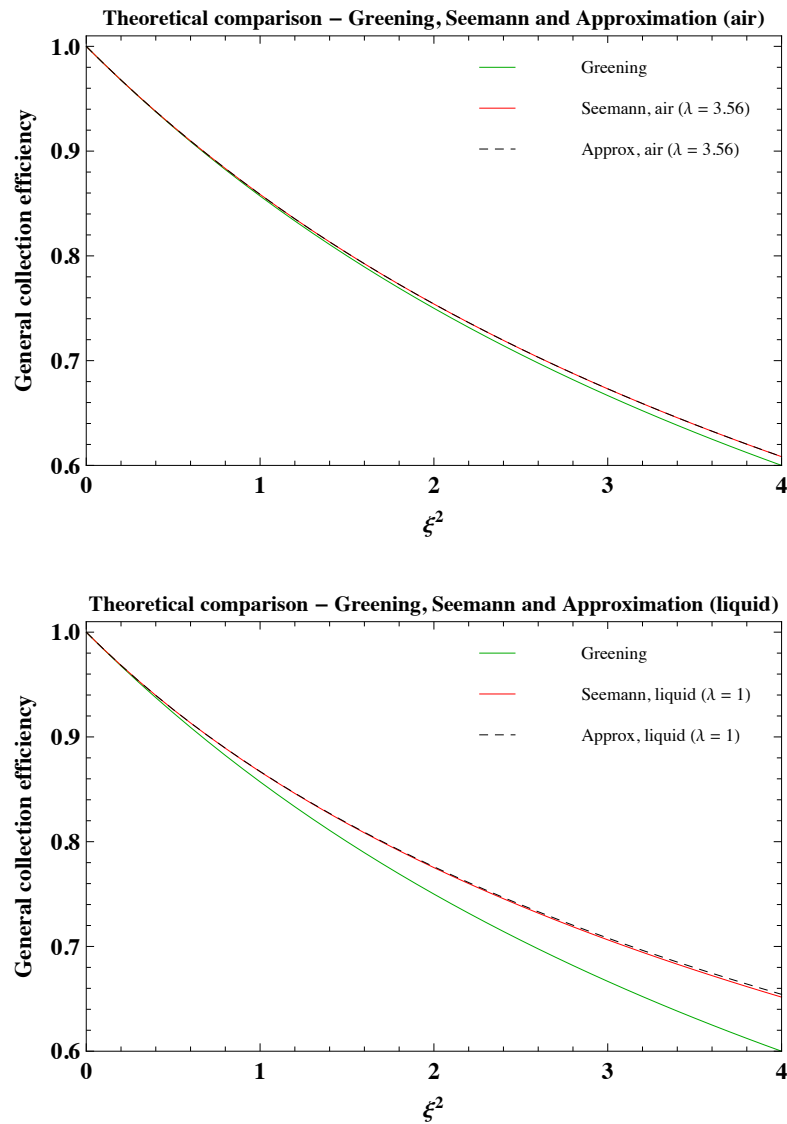
Figure 4.2.2. Theoretical comparison between the general collection efficiencies according to Seemann (1912), Greening (1964), and the relation derived in paper IV (4.2.31).

As seen in figure 4.2.2, the theoretical agreement between the approximation derived in paper IV and the original expression according to Seemann is much better than that proposed by Greening for both air ($\lambda = 3.56$) and liquid ($\lambda = 1$) employed as the sensitive media in an ionization chamber.

4.3. General recombination in pulsed beams

Boag (1950) derived an expression for the general collection efficiency for ionization chambers employed for measurements in pulsed beams. Here, a plane parallel air-filled ionization chamber is considered with an applied voltage U, and plate separation h irradiated by a pulsed beam that yields a charge density per pulse r. In the derivation it is assumed that the radiation pulse is short compared to the average ion transit time within the measurement volume, i.e. that the measurement signal pulses are well separated. Similarly as in the treatment of continuous beams, k_1 and k_2 represent the mobilities of positive and negative ions, respectively, and α the general recombination rate constant.

Boag defines three distinct regions in the measurement volume between the electrodes immediately after an absorbed dose has been delivered to the sensitive media from a single pulse, leading to a charge density r. There is a region defined by a width ξ_1, which only contains negative ions. The edge of this region is moving towards the negative electrode with a velocity $k_1 E_\xi$, where E_ξ is the collecting electric field strength at the edge of the region. Furthermore, there is an overlap in the centre of the measurement volume, which consists of a region containing ions of both signs in equal number per unit volume (n). In this region, recombination between positive and negative ions will occur at a rate given by the relation

$$\frac{dn}{dt} = -\alpha \, n^2,$$
(4.3.1)

which has the following solution

$$n = \frac{n_0}{(1 + \alpha \, n_0 \, t)}.$$
(4.3.2)

Here, n_0 represents the initial amount of ions created per unit volume and pulse, and the collecting electric field strength is assumed to be uniform in the overlap region. Analogously to the region moving towards the negative electrode, there is also a corresponding region containing only positive ions that moves with an edge velocity of $k_2 E_\xi$ towards the positive electrode.

As an approximation Boag considers the case of a negligible space charge effect, i.e. the collecting electric field strength is assumed to be constant, and equal to U/h, in all points between the electrodes during the time it takes to collect the created charge. In the present terminology, the temporal rate of change of the overlap region may thus be formulated as

$$\frac{d}{dt}(\xi_1 + \xi_2) = (k_1 + k_2)\, E_\xi = (k_1 + k_2)\frac{U}{h}, \tag{4.3.3}$$

which has the following solution

$$\xi_1 + \xi_2 = (k_1 + k_2)\frac{U\,t}{h}. \tag{4.3.4}$$

Furthermore, the positive and negative regions will meet when the overlap region has vanished ($\xi_1 + \xi_2 = h$), i.e. the overlap region has a lifetime (T) after the radiation pulse has ionized the media corresponding to

$$T = \frac{h^2}{(k_1 + k_2)\, U}. \tag{4.3.5}$$

By employing (4.3.2) and (4.3.3) the total amount of ions per unit area of each sign escaping recombination into the positive and negative regions, respectively, can be formulated as

$$R_{esc} = \int_0^T \frac{n_0}{(1 + \alpha\, n_0\, t)}(k_1 + k_2)\frac{U}{h}\, dt = \frac{(k_1 + k_2)\, U}{\alpha\, h}\, [ln(1 + \alpha\, n_0\, t)]_0^T =$$

$$= \left\{ T = \frac{h^2}{(k_1 + k_2)\, U} \right\} = \frac{(k_1 + k_2)\, U}{\alpha\, h} \ln\left(1 + \alpha\, n_0 \frac{h^2}{(k_1 + k_2)\, U}\right). \tag{4.3.6}$$

Finally, the general collection efficiency for pulsed beams according to the work by Boag can be expressed as the ratio of ions escaping recombination (R_{esc}) and the total amount of ions created per unit area and pulse ($n_0\, h$), which corresponds to

$$f = \frac{R_{esc}}{n_0\, h} = \frac{1}{u}\, \ln(1 + u), \tag{4.3.7}$$

where

$$u = \frac{\alpha\, n_0\, h^2}{(k_1 + k_2)\, U} = \frac{\alpha}{e\,(k_1 + k_2)}\frac{r\, h^2}{U}. \tag{4.3.8}$$

Relations (4.3.7) and (4.3.8) are equal to the result previously derived by Langevin (1902) in studies of the general recombination rate constant.

Boag also discusses possible detrimental effects from distortion of the collecting electric field on this treatment of the general collection efficiency in pulsed beams. It is concluded that the space charge effect should be of negligible importance for air-filled ionization chambers employed for measurements in pulsed beams due to two key arguments. Firstly, Boag deduces that for a large dose per pulse, the rate of recombination in the

overlap region is also large and the majority of the recombination will occur in a very short period of time. Secondly, the total amount of recombination per unit time will be proportional to the width of the overlap region, which is the largest immediately after the pulse has ionized the sensitive media in an ionization chamber. Whether or not the ions will recombine should therefore be strongly dependent on what happens when the width of the positive and negative regions is small, i.e. for a small space charge effect.

While the derivation of the general collection efficiency for pulsed beams according to Boag is argumentative, and the result may thus be considered as semi-empirical, it has been extensively verified for air-filled ionization chambers. The results from the work by Boag are used in the two-voltage method for the correction of general recombination losses in air-filled ionization chambers employed in pulsed photon and electron beams (TRS-398, IAEA 2000). In the present work, results from the work by Boag have been used to model general recombination in LICs in the three-voltage and two-dose-rate methods for pulsed beams investigated in paper III.

5. Experimental quantification of general recombination

In reference as well as clinical radiation dosimetry employing air-filled ionization chambers, corrections for general recombination are achieved by experimental means. Due to uncertainties in the exact construction of a given ionization chamber and the experimental conditions, direct application of a theoretical model is unlikely to be as accurate as a well designed experimental method for a given measurement situation. The two-voltage method is presently the recommended procedure for general recombination correction for air-filled ionization chambers employed for radiation dosimetry for photon and electron beams (TRS-398, IAEA 2000).

Due to the presence of both initial and general recombination in liquids, the two-voltage method cannot be used for LICs. A three-voltage method for general recombination correction for LICs has been proposed by Pardo-Montero and Gómez (2009), which models initial and general recombination explicitly. The two-dose-rate method for general recombination correction for liquid ionization chambers, which was first proposed by Tölli *et al* (2010) for pulsed beams, has been extended in the present work to encompass continuous beams (paper I and II).

In the following subsections the shortcomings of employing the two-voltage method for LICs is explained. Furthermore, the three-voltage and two-dose-rate methods are also detailed and analysed.

5.1. The two-voltage method

The two-voltage method for general recombination correction for air-filled ionization chambers has been derived for both pulsed (Boag and Currant, 1980) and continuous radiation beams (Almond, 1981). As the name implies, the correction for general recombination is achieved by recording ionization chamber readings (Q_1, Q_2) at two different applied voltages (U_1, U_2).

As shown by Boag and Currant, the work by Boag (1950) can be employed to model general recombination in a two-voltage method for pulsed beams according to relation (4.3.7). The general collection efficiency $f(U_i)$ for applied voltages U_1 and U_2 can be formulated as

$$f(U_1) = \frac{Q_1}{Q_0} = \frac{1}{u_1}\ln(1 + u_1), \tag{5.1.1}$$

$$f(U_2) = \frac{Q_2}{Q_0} = \frac{1}{u_2}\ln(1 + u_2). \tag{5.1.2}$$

Here, Q_0 represents the total amount of charge created by ionization, i.e. before recombination losses. Taking the ratio of (5.1.1) and (5.1.2) yields

$$\frac{f(U_1)}{f(U_2)} = \frac{Q_1}{Q_2} = \frac{u_2 \ln(1+u_1)}{u_1 \ln(1+u_2)} = \left\{u_2 = u_1\left(\frac{U_1}{U_2}\right)\right\} = \frac{U_1}{U_2}\frac{\ln(1+u_1)}{\ln\left(1+u_1\left(\frac{U_1}{U_2}\right)\right)}. \tag{5.1.3}$$

The two-voltage method for pulsed beams is thus based on performing measurements with an ionization chamber at two applied voltages, numerically solving u_1 from (5.1.3) and finally determining the general collection efficiency for the primary applied voltage $\left(f(U_1)\right)$ from (5.1.1). Alternatively, and a common course of action in clinical radiation dosimetry, a polynomial solution for the correction factor (k_s) for general recombination according to the two-voltage method for pulsed beams has been given in TRS-398 (IAEA, 2000). The polynomial is expressed as

$$k_s = a_0 + a_1\left(\frac{Q_1}{Q_2}\right) + a_2\left(\frac{Q_1}{Q_2}\right)^2, \tag{5.1.4}$$

where values of the constants a_i are tabulated for different ratios of applied voltages for pulsed, as well as and pulsed and scanned beams (TRS-398, IAEA 2000).

For continuous beams, the two-voltage method is based on the expression for the general collection efficiency proposed by Greening (1964). Here, a quite different approach than that for pulsed beams can be used, where the general collection efficiency at an applied voltage U_1 is expressed as

$$f(U_1) = \frac{Q_1}{Q_0} = \frac{1}{1+\frac{1}{6}\xi_1^2}. \tag{5.1.5}$$

Furthermore, employing that the total amount of charge created per unit time and volume can be written as $q_0 = Q_0/(V\,t)$ and the definition of the parameter ξ^2 (4.2.28), we can reformulate (5.1.5) as

$$\frac{1}{Q_1} = \frac{1}{Q_0} + \frac{C}{U_1^2}, \tag{5.1.6}$$

where the constant C is given by

$$C = \frac{m^2 h^4}{6\,V\,t}. \tag{5.1.7}$$

Here, V represents the measurement volume and t the measurement time. If two different applied voltages are chosen, e.g. $U_2 = U_1/4$, we can use (5.1.6) to express the general collection efficiency for the primary applied voltage $\left(f(U_1)\right)$ according to the two-voltage method for continuous beams as

$$f(U_1) = \frac{Q_1}{Q_0} = \frac{16}{15} - \frac{1}{15}\frac{Q_1}{Q_2}. \tag{5.1.8}$$

The two-voltage methods discussed here have been employed to determine the general recombination losses for the air-filled reference ionization chambers used in continuous beams (papers I-IV), as well as pulsed beams (paper III).

5.1.1. The two-voltage method and liquid ionization chambers

Since the charge reading from a LIC is affected by both initial and general recombination, the two-voltage method is not well suited to determine general recombination losses for these types of chambers. While there is no general theory for initial recombination in liquids it is known that this process depends on the collecting electric field strength, e.g. as described by Onsager (1938), and a two-voltage method derived for LICs will therefore be insufficient. An interesting discussion on this subject for plane parallel LICs can be found in the work by Pardo-Montero and Gómez (2009). Here, the free-ion yield $\left(G_{fi}\right)$ according to Mozumder's treatment (1974a) of the Onsager theory (1938) is considered for a LIC containing isooctane under the assumption that G_{fi} has an approximately linear relationship to the collecting electric field, as discussed in section 4.1,

$$G_{fi} \approx G_{fi}^0(1 + a\,E). \tag{5.1.1.1}$$

Pardo-Montero and Gómez (2009) suggests that the parameter a in (5.1.1.1) should be well approximated by the inverse of the Onsager field (E_0), but the authors recommend an experimental determination of a. Furthermore, considering a hypothetical case of no general recombination and employing (5.1.1.1), the charge reading from a LIC for an applied voltage U_i may be expressed as

$$Q_i(U_i) = Q_0(1 + c\,U_i), \tag{5.1.1.2}$$

where Q_0 is the amount of charge created escaping initial recombination, and $c = a/h$, where h is the electrode separation.

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The amount of charge escaping initial recombination formulated according to relation (5.1.1.2) may be used together with the general collection efficiency according to Greening (1964) for continuous beams, which yields

$$f_c(U_1) = \frac{Q_1}{Q_0 \, (1 + c \, U_1)} = \left(1 + \frac{A_c \, (1 + c \, U_1)}{U_1^2}\right)^{-1},$$

(5.1.1.3)

where Q_1 represents a LIC reading at an applied voltage U_1, and

$$A_c = \frac{\alpha \, q_0 \, h^4}{6 \, k_1 \, k_2}.$$

(5.1.1.4)

A two-voltage method for continuous beams can thus be derived from (5.1.1.3), by taking the ratio $f_c(U_1)/f_c(U_2)$, which by manipulation of the resulting expression leads to

$$f_c^{2VM}(U_1) = \frac{(1 + c \, U_2)(U_2^2 \, Q_1 - U_1^2 \, Q_2)}{(1 + c \, U_1) \, U_2^2 \, Q_2 - (1 + c \, U_2) \, U_1^2 \, Q_2}.$$

(5.1.1.5)

A similar argument can be made for the case of pulsed beams by employing the work by Boag (1950) and making the substitution $r = r_0 \, (1 + c \, U)$, where r is the amount of charge created per unit volume and pulse escaping initial recombination for an applied voltage U. This yields the following expression for the general collection efficiency for pulsed beams

$$f_p(U_1) = \frac{Q_1}{Q_0 \, (1 + c \, U_1)} = \frac{U_1}{A_p \, (1 + c \, U_1)} \ln\left(1 + \frac{A_p}{U_1}(1 + c \, U_1)\right),$$

(5.1.1.6)

where

$$A_p = \frac{\alpha \, r_0 \, h^2}{e \, (k_1 + k_2)}.$$

(5.1.1.7)

As shown by Pardo-Montero and Gómez (2009), by employing a second order Taylor expansion of the logarithmic term in (5.1.1.6), the ratio $f_p(U_1)/f_p(U_2)$ can be formulated, which by manipulation yields a two-voltage method expressed as

$$f_p^{2VM}(U_1) = \frac{(1 + c \, U_2)^2 \, U_1 \, Q_1 - (1 + c \, U_1)(1 + c \, U_2) \, U_2 \, Q_1}{(1 + c \, U_2)^2 \, U_1 \, Q_1 - (1 + c \, U_1)^2 \, U_2 \, Q_2}.$$

(5.1.1.8)

The two-voltage methods based on explicit modelling of both initial and general recombination given by (5.1.1.5) and (5.1.1.8) for continuous and pulsed beams, respectively, both suffer from that the parameter c is not well known.

5.2. The three-voltage method

In order to experimentally solve the issues with a two-voltage method for LICs based on Mozumder's treatment (1974a) of the Onsager theory (1938), Pardo-Montero and Gómez (2009) proposed a three-voltage method to enable an experimental determination of the parameter c in relations (5.1.1.3) and (5.1.1.6).

For continuous beams, the formalism of the three-voltage method based on the general collection efficiency according to Greening (1964) leads to an equation system based on LIC readings Q_i for applied voltages U_i $(i = 2, 3)$ on the form

$$\left(\frac{Q_i}{1+c\,U_i}\right)\left(1 + \frac{A_c}{U_i^2}(1 + c\,U_i)\right) - \left(\frac{Q_1}{1+c\,U_1}\right)\left(1 + \frac{A_c}{U_1^2}(1 + c\,U_1)\right) = 0. \qquad (5.2.1)$$

The equation system (5.2.1) is solved for the parameters c and A_c, which have their previous definitions, and the general collection efficiency for continuous beams is then determined for the primary voltage $\left(f_c(U_1)\right)$ from relation (5.1.1.3).

For pulsed beams, the three-voltage method employs the theory by Boag (1950) to model general recombination, and by the three-voltage formalism an equation system based on LIC readings Q_i at applied voltages U_i $(i = 2, 3)$ is expressed as

$$Q_i\,U_1 \ln\left(1 + \frac{A_p}{U_1}(1 + c\,U_1)\right) - Q_1\,U_i \ln\left(1 + \frac{A_p}{U_i}(1 + c\,U_i)\right) = 0. \qquad (5.2.2)$$

To determine the general collection efficiency for pulsed beams, the equation system (5.2.2) is solved for the parameters c and A_p, and $f_p(U_1)$ may then be determined from (5.1.1.6).

The three-voltage method was investigated in paper III, for both continuous and pulsed beams. In comparison to the two-dose-rate method, severe problems with the accuracy and robustness of the three-voltage method were identified. Therefore, an extension of the modelling of initial recombination as second- instead of first-order polynomials (Onsager 1938, Mozumder 1974a) was also evaluated in paper III according to the three-voltage methodology for both continuous and pulsed beams as

$$q = q_0 \left(1 + c_1 \, U + c_2 \, U^2\right), \tag{5.2.3}$$

$$r = r_0 \left(1 + c_1 \, U + c_2 \, U^2\right). \tag{5.2.4}$$

Employing these relations an extended modelling of initial recombination may be achieved through the parameters c_1 and c_2. Since an additional unknown parameter is introduced here, a LIC reading is required from yet another applied voltage to determine the general collection efficiency. Analogously to the formalism employed in the three-voltage method, the resulting equation system is based on LIC readings Q_i from measurements performed at applied voltages U_i $(i = 2, 3, 4)$. The general collection efficiency for the primary applied voltage $\left(f_{c,p}(U_1)\right)$ may be calculated from experimentally determined values of the parameters $A_{c,p}$, c_1 and c_2. In order to achieve this, the three-voltage methodology for the general collection efficiency according to (5.1.1.3) and (5.1.1.6) can be trivially modified with the extended modelling in (5.2.3) and (5.2.4) for continuous and pulsed beams, respectively.

5.2.1. Analysis of the three-voltage method

In the present work, the performance of the three-voltage method has been investigated with experimental data from continuous beams of 120 kV x-rays (paper I), as well as pulsed beams of 20 MeV electrons (Tölli *et al*, 2010) and compared to the two-dose-rate method (paper III). The veracity of the results from the respective methods for general recombination correction in paper III were determined by the signal to dose rate linearity in the corrected LIC to NACP-02 reading ratios. Furthermore, each method was evaluated according to the spread in the resulting general collection efficiencies given by combinations of LIC readings from different dose rates (the two-dose-rate method) and different applied voltages (the three-voltage method).

As reported in paper III, problems were identified in the results from the three-voltage method, including large deviations depending on the voltage tuple chosen from the measurements (U_1, U_2, U_3). In the investigation of the three-voltage method, issues with convergence in the numerical methods were also observed. General collection efficiencies determined according to the three-voltage method and examples of the variations in the results depending on the voltage tuple chosen from the experiments involving continuous beams for the LIC containing isooctane are shown in table 5.2.1.1 and figure 5.2.1.1, respectively.

Table 5.2.1.1. General collection efficiencies determined according to the three-voltage method for the microLion LIC containing isooctane for the experiments involving continuous beams of 120 kV x-rays. Values in the parenthesis represent one relative standard deviation.

| Dose rate (Gy min^{-1})	100 V	300 V	500 V	700 V	900 V
2.2	0.858 (1.6)	0.964 (1.9)	0.983 (0.9)	0.991 (0.5)	0.994 (0.3)
4.4	0.827 (2.2)	0.954 (2.4)	0.982 (1.1)	0.989 (0.6)	0.993 (0.4)
6.5	0.803 (2.3)	0.948 (2.5)	0.979 (1.0)	0.988 (0.6)	0.991 (0.4)
8.7	0.784 (1.9)	0.947 (2.1)	0.976 (0.8)	0.986 (0.5)	0.990 (0.3)
10.9	0.764 (2.3)	0.940 (2.6)	0.975 (1.1)	0.985 (0.6)	0.990 (0.4)
13.0	0.748 (2.7)	0.934 (3.0)	0.973 (1.5)	0.985 (0.8)	0.990 (0.5)
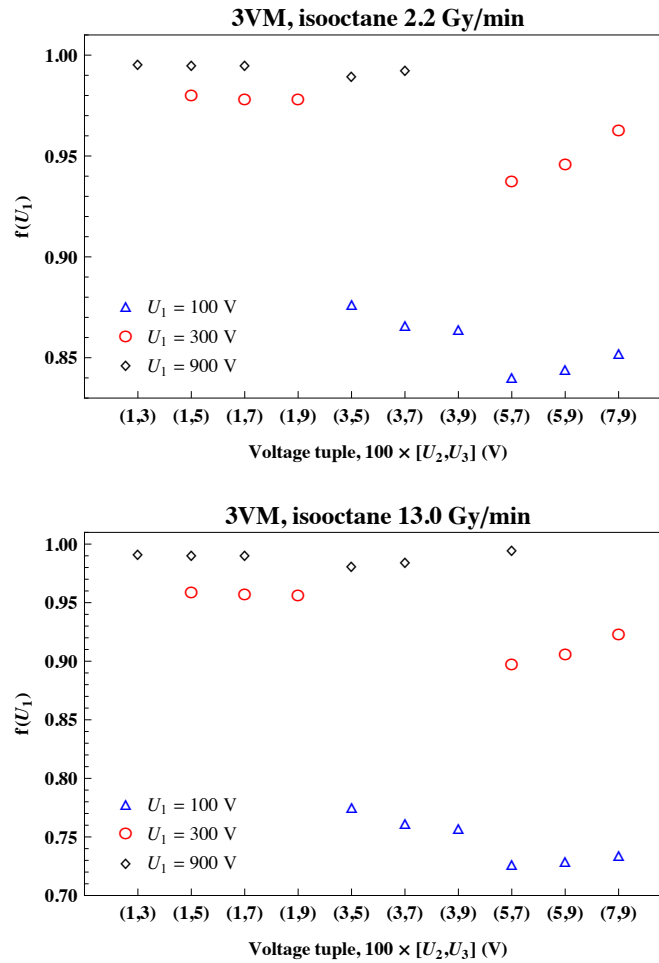
Figure 5.2.1.1. Examples of results from the three-voltage method (3VM) for the microLion LIC containing isooctane for the lowest and highest dose rates, respectively, from the experiments involving continuous beams of 120 kV x-rays. The applied voltages to the LIC shown here are 100, 300 and 900 V.

The general collection efficiencies according to the three-voltage method and examples of the variations of results depending on the voltage tuple chosen from the experiments involving continuous beams for the LIC containing tetramethylsilane are shown in table 5.2.1.2 and figure 5.2.1.2, respectively.

Table 5.2.1.2. General collection efficiencies determined according to the three-voltage method for the microLion LIC containing tetramethylsilane for the experiments involving continuous beams of 120 kV x-rays. Values in the parenthesis represent one relative standard deviation.

Dose rate (Gy min^{-1})	100 V	300 V	500 V	700 V	900 V
2.2	0.772 (4.0)	0.931 (4.2)	0.969 (1.6)	0.982 (0.9)	0.987 (0.6)
4.4	0.715 (4.3)	0.917 (4.4)	0.962 (1.8)	0.977 (1.0)	0.985 (0.7)
6.5	0.674 (4.8)	0.903 (5.0)	0.956 (1.9)	0.974 (1.1)	0.982 (0.7)
8.7	0.638 (5.1)	0.891 (5.4)	0.952 (2.0)	0.972 (1.1)	0.981 (0.7)
10.9	0.611 (5.2)	0.883 (5.5)	0.949 (2.1)	0.971 (1.1)	0.980 (0.7)
13.0	0.585 (5.3)	0.874 (5.6)	0.944 (2.1)	0.967 (1.1)	0.978 (0.7)
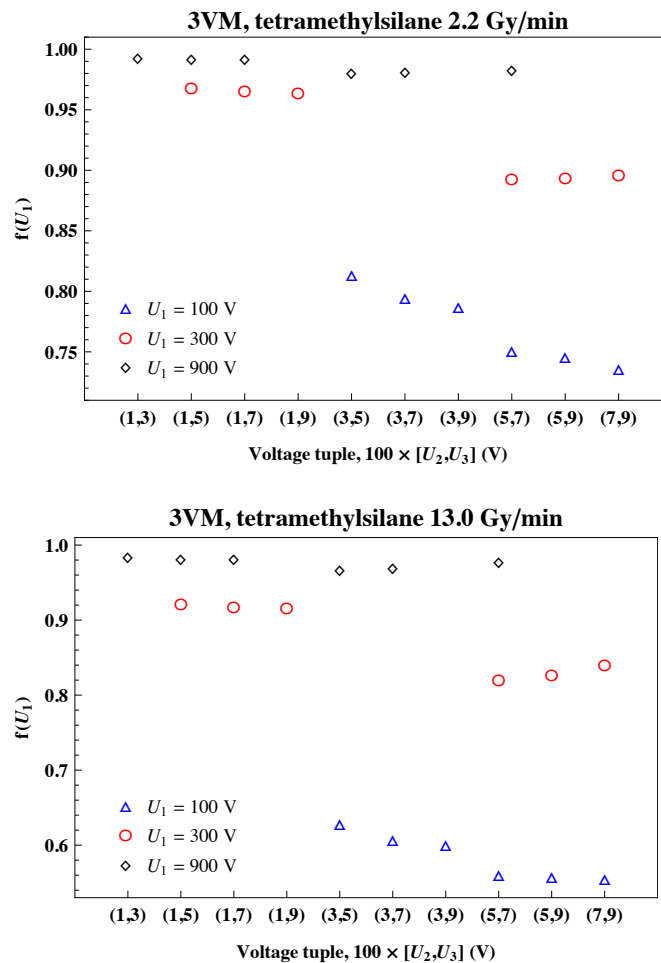
Figure 5.2.1.2. Examples of results from the three-voltage method (3VM) for the microLion LIC containing tetramethylsilane for the lowest and highest dose rates, respectively, from the experiments involving continuous beams of 120 kV x-rays. The applied voltages to the LIC shown here are 100, 300 and 900 V.

As seen in figure 5.2.1.1 and 5.2.1.2, the large relative standard deviations observed in table 5.2.1.1 and 5.2.1.2 are due to variations in the results from the three-voltage method depending on the voltage tuple chosen from the measurement data (U_1, U_2, U_3). Furthermore, the results from the three-voltage method for continuous beams were poorer for the LIC containing tetramethylsilane compared to isooctane. There were also convergence issues with the numerical solutions to the three-voltage method for measurement data from the dose rate 2.2 Gy min^{-1} for the LIC containing isooctane. When compared to the signal to dose rate linearity resulting from

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corrections according to the two-dose-rate method, the three-voltage method only achieves equivalent corrections for continuous beams for very small general recombination losses (< 1%).

The extended three-voltage method for continuous beams, as described by (5.2.3), was also analysed in paper III. It was found that a second-order polynomial modelling of initial recombination gave comparable results to the original three-voltage method. The results could be interpreted as slightly improved for the LIC containing tetramethylsilane, while the differences were within the experimental uncertainties for isooctane.

General collection efficiencies determined according to the three-voltage method for pulsed beams and examples of the variations of results depending on the voltage tuple chosen from the experiments involving pulsed beams of 20 MeV electrons for the LIC containing isooctane are shown in table 5.2.1.3 and figure 5.2.1.3, respectively.

Table 5.2.1.3. General collection efficiencies determined according to the three-voltage method for the microLion LIC containing isooctane for the experiments involving pulsed beams of 20 MeV electrons. Values in the parenthesis represent one relative standard deviation.

Dose per pulse (mGy pulse^{-1})	300 V	500 V	700 V	900 V
0.14	0.824 (4.0)	0.849 (7.2)	0.866 (5.5)	0.878 (4.1)
0.28	0.822 (2.9)	0.853 (5.3)	0.872 (4.0)	0.884 (3.0)
0.43	0.807 (3.4)	0.840 (6.1)	0.859 (4.7)	0.873 (3.5)
0.57	0.811 (2.5)	0.847 (4.6)	0.867 (3.5)	0.881 (2.6)
0.78	0.803 (2.7)	0.840 (5.0)	0.861 (3.8)	0.874 (2.9)
1.2	0.787 (3.5)	0.823 (6.3)	0.845 (4.9)	0.860 (3.7)
2.6	0.731 (3.9)	0.777 (7.0)	0.804 (5.4)	0.822 (4.1)
4.2	0.683 (3.6)	0.738 (6.5)	0.770 (5.1)	0.791 (3.8)
5.7	0.638 (2.5)	0.704 (4.5)	0.742 (3.5)	0.767 (2.6)
7.8	0.594 (4.4)	0.658 (7.9)	0.695 (6.2)	0.721 (4.7)

3VM, isooctane 0.14 mGy/pulse

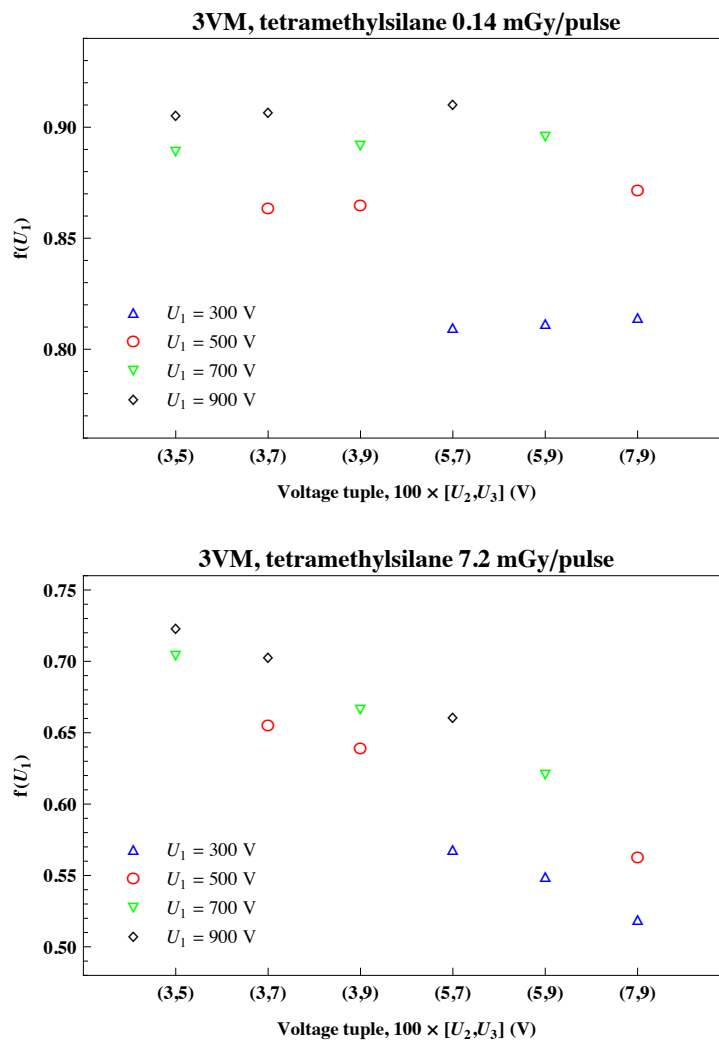
3VM, isooctane 7.8 mGy/pulse
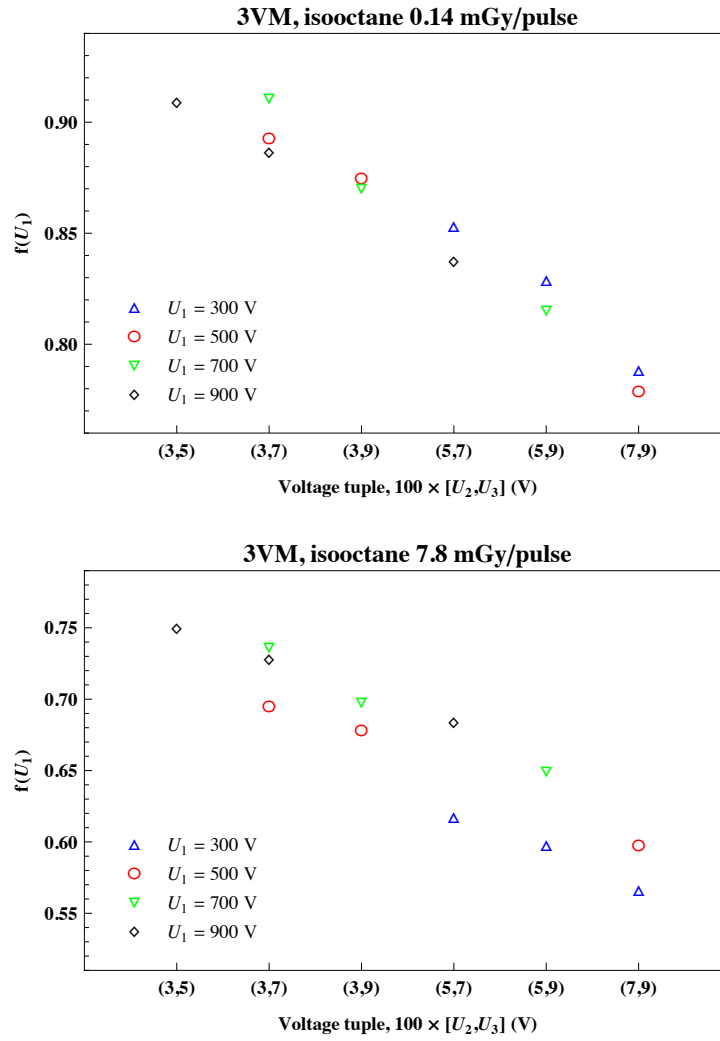
Figure 5.2.1.3. Examples of results from the three-voltage method (3VM) for the microLion LIC containing isooctane for the lowest and highest dose per pulse, respectively, from the experiments involving pulsed beams of 20 MeV electrons.

The general collection efficiencies according to the three-voltage method and examples of the variations of results depending on the voltage tuple chosen from the experiments involving pulsed beams of 20 MeV electrons for the LIC containing tetramethylsilane are shown in table 5.2.1.4 and figure 5.2.1.4, respectively.

Table 5.2.1.4. General collection efficiencies determined according to the three-voltage method for the microLion LIC containing tetramethylsilane for the experiments involving pulsed beams of 20 MeV electrons. Values in the parenthesis represent one relative standard deviation.

Dose per pulse (mGy pulse^{-1})	300 V	500 V	700 V	900 V
0.14	0.812 (0.3)	0.867 (0.5)	0.893 (0.4)	0.908 (0.3)
0.28	0.791 (3.2)	0.832 (5.6)	0.857 (4.2)	0.873 (3.1)
0.43	0.782 (3.3)	0.825 (5.7)	0.851 (4.3)	0.868 (3.2)
0.56	0.782 (3.1)	0.825 (5.5)	0.851 (4.1)	0.868 (3.0)
0.73	0.767 (2.9)	0.815 (5.1)	0.843 (3.8)	0.861 (2.8)
1.3	0.743 (3.2)	0.795 (5.6)	0.825 (4.2)	0.845 (3.1)
2.7	0.682 (2.6)	0.747 (4.6)	0.784 (3.5)	0.808 (2.5)
4.3	0.620 (3.3)	0.691 (5.8)	0.732 (4.5)	0.761 (3.3)
5.3	0.569 (1.7)	0.653 (3.0)	0.702 (2.3)	0.734 (1.7)
7.2	0.546 (4.5)	0.620 (8.0)	0.665 (6.2)	0.696 (4.6)

3VM, tetramethylsilane 0.14 mGy/pulse

3VM, tetramethylsilane 7.2 mGy/pulse

Figure 5.2.1.4. Examples of results from the three-voltage method (3VM) for the microLion LIC containing tetramethylsilane for the lowest and highest dose per pulse, respectively, from the experiments involving pulsed beams of 20 MeV electrons.

As seen in figure 5.2.1.3 and 5.2.1.4, the large relative standard deviations observed in table 5.2.1.3 and 5.2.1.4 are due to very strong trends in the results depending on the voltage tuple chosen from the experimental data (U_1, U_2, U_3). Furthermore, similarly as for the case of continuous beams, the results are generally worse for tetramethylsilane as compared to isooctane for the three-voltage method. A notable exception is the lowest dose per pulse (0.14 mGy pulse[-1]) for the LIC containing tetramethylsilane, which represents the only results from the three-voltage method for pulsed beams

that do not display a very strong trend depending on the voltage tuple chosen from the experimental data.

The extended three-voltage method for pulsed beams, as described by (5.2.4) was also analysed in paper III. It was found that a second-order polynomial modelling of initial recombination gave even poorer results then the original three-voltage method. Here, severe issues with convergence in the numerical solutions were observed, and the resulting general collection efficiencies displayed an even larger spread than the original three-voltage method.

The series expansion approach to the three-voltage method, which entails a Taylor-expansion of the logarithmic term in (5.2.2) as described by Pardo-Montero and Gómez (2009), yields very poor results for the experimental data from pulsed beams of 20 MeV electrons. For a low dose per pulse, results from the series expansion approach are comparable to the original three-voltage method for pulsed beams. Furthermore, the results deviate increasingly with an increasing dose per pulse, indicating insufficiency in this treatment of the three-voltage methodology. Examples of results from the series expansion approach to the three-voltage method are shown in figure 5.3.1.1.

5.3. The two-dose-rate method

A two-dose-rate method for general recombination correction for LICs was first proposed by Tölli *et al* (2010), in an application for pulsed beams by modelling general recombination according to the work by Boag (1950). The two-dose-rate method has a similar approach as the two-voltage method, but as the name implies the correction for general recombination is achieved by measurements at two separate dose rates, or dose per pulse. In contrast to the three-voltage method, where initial recombination is modelled explicitly, the two-dose-rate method handles the combined action of initial and general recombination through a separation of these processes.

The two-dose-rate method for pulsed beams, based on a modelling of general recombination according to the work by Boag (1950), is derived from the relation

$$f(d_i) = \frac{Q_M(d_i)}{Q_0(d_i)} = \frac{1}{u(d_i)} \ln\big(1 + u(d_i)\big), \tag{5.3.1}$$

where $Q_0(d_i)$ and $Q_M(d_i)$ represents the total amount of charge created in the measurement volume escaping initial recombination and the measured charge, respectively. Taking the ratio of the general collection efficiencies at dose rates d_1 and d_2 yields

$$\frac{Q_M(d_1)}{Q_M(d_2)} \frac{Q_0(d_2)}{Q_0(d_1)} = \frac{u(d_2)}{u(d_1)} \frac{\ln\big(1+u(d_1)\big)}{\ln\big(1+u(d_2)\big)}. \tag{5.3.2}$$

The definition of the parameter $u(d_i)$ from the work by Boag (1950), as given by relation (4.3.8), can be employed to express

$$u(d_2) = \frac{\alpha}{e\,(k_1+k_2)} \frac{r(d_2)\,h^2}{U} = \frac{\alpha}{e\,(k_1+k_2)} \frac{r(d_1)\,h^2}{U} \frac{r(d_2)}{r(d_1)} = u(d_1) \frac{Q_0(d_2)}{Q_0(d_1)}. \tag{5.3.3}$$

Here, the relation $r(d_i) = Q_0(d_i)/V$ has been used, where V represents the measurement volume. Employing (5.3.3), relation (5.3.2) can be reformulated as

$$\frac{Q_M(d_1)}{Q_M(d_2)} = \frac{\ln\big(1+u(d_1)\big)}{\ln\left(1+\frac{Q_0(d_2)}{Q_0(d_1)}u(d_1)\right)}. \tag{5.3.4}$$

Furthermore, Tölli *et al* (2010) considered the ratio

$$\frac{Q_0(d_2)}{Q_0(d_1)} = \frac{q_0(d_2)}{q_0(d_1)} \frac{f_I(d_1,U)}{f_I(d_2,U)}, \tag{5.3.5}$$

where $q_0(d_i)$ represents the total amount of charge created per unit volume and dose per pulse d_i, and $f_I(d_i, U)$ the escape probability from initial recombination at a dose per pulse d_i and applied voltage U. It was then deduced that since initial recombination is independent of the dose rate, relation (5.3.5) reduces to

$$\frac{Q_0(d_2)}{Q_0(d_1)} = \frac{q_0(d_2)\, f_I(U)}{q_0(d_1)\, f_I(U)} = \frac{q_0(d_2)}{q_0(d_1)}. \tag{5.3.6}$$

The right hand side of (5.3.6) is equal to the ratio of the charge initially created in a LIC measurement volume and should thus be well approximated by a ratio of charge measured by a reference air-filled ionization chamber corrected for perturbations according to TRS-398 (IAEA, 2000). Tölli *et al* (2010) thus expressed the two-dose-rate method for pulsed beams based on the work by Boag (1950), employing a NACP-02 ionization chamber as a monitor, as

$$\frac{Q_M(d_1)}{Q_M(d_2)} = \frac{\ln(1+u(d_1))}{\ln\left(1+\frac{Q_{NACP}(d_2)}{Q_{NACP}(d_1)}u(d_1)\right)}, \tag{5.3.7}$$

where $Q_M(d_i)$ represents a LIC reading and $Q_{NACP}(d_i)$ a NACP-02 chamber reading at dose rate d_i, respectively. To determine the general collection efficiency for a LIC employed for measurements in pulsed beams, $u(d_1)$ is solved numerically from (5.3.7) and $f(d_1)$ may then be calculated according to (5.3.1).

In paper I, the two-dose-rate method was applied to continuous beams by employing the expression proposed by Greening (1964) to model general recombination. Here, the general collection efficiency for a dose rate d_1 and applied voltage U is expressed as

$$f(d_1, U) = \frac{Q_M(d_1)}{Q_0(d_1)} = \frac{1}{1+\frac{1}{6}\xi_1^2}, \tag{5.3.8}$$

where the different parameters have their previously defined meanings. Employing the ratio $f(d_1, U)/f(d_2, U)$, which can be expressed as

$$\frac{Q_M(d_1)}{Q_M(d_2)}\frac{Q_0(d_2)}{Q_0(d_1)} = \frac{\left(1+\frac{1}{6}\xi_2^2\right)}{\left(1+\frac{1}{6}\xi_1^2\right)}, \tag{5.3.9}$$

and that $q(d_i) = Q_0(d_i)/(V\,t)$, where V represents the measurement volume and t the measurement time, we can formulate

$$\xi_2^2 = \left(m\frac{h^2}{U}\right)^2 \frac{Q_0(d_2)}{V\,t} = \left(m\frac{h^2}{U}\right)^2 \frac{Q_0(d_1)}{V\,t}\frac{Q_0(d_2)}{Q_0(d_1)} = \frac{Q_0(d_2)}{Q_0(d_1)}\,\xi_1^2. \tag{5.3.10}$$

Furthermore, by combining (5.3.9) and (5.3.10), the parameter ξ_1^2 can be expressed as

$$\xi_1^2 = \frac{\left(\frac{Q_{NACP}(d_1)}{Q_{NACP}(d_2)} - \frac{Q_M(d_1)}{Q_M(d_2)}\right)}{\frac{1}{6}\left(\frac{Q_M(d_1)}{Q_M(d_2)}-1\right)}. \tag{5.3.11}$$

In paper I, an argument similar to that made by Tölli *et al* (2010) was used in the separation of initial and general recombination (5.3.6), as well as the incorporation of readings from a reference chamber $\left(Q_0(d_i) = Q_{NACP}(d_i)\right)$. An analytical solution of ξ_1^2 according to (5.3.11) from charge readings from a LIC and a reference chamber then yields the general collection efficiency for a LIC employed for measurements in continuous beams from relation (5.3.8).

As shown in paper IV, a robust approximation of the original expression for the general collection efficiency by Seemann (1912) can be derived. The robustness of this approximation is not only mathematical, since the media specific parameter λ (4.2.16) is retained in the final expression. Furthermore, the parameter λ has been shown to be approximately equal to unity for a dielectric liquid in the work by Debye (1942). By employing the approximation derived in paper IV (4.2.31) in the two-dose-rate methodology, the following expression can be formulated

$$\frac{Q_M(d_1)}{Q_M(d_2)}\frac{Q_{NACP}(d_2)}{Q_{NACP}(d_1)} =$$

$$= \frac{\frac{1}{2}-\frac{15}{\xi_1^2\,(4-\lambda)}-\frac{5}{2\,(4-\lambda)}+\sqrt{\left(\frac{30}{\xi_1^2\,(4-\lambda)}+\frac{5}{(4-\lambda)}-1\right)^2+\frac{120}{\xi_1^2\,(4-\lambda)}}}{\frac{1}{2}-\frac{15}{\frac{Q_{NACP}(d_2)}{Q_{NACP}(d_1)}\xi_1^2\,(4-\lambda)}-\frac{5}{2\,(4-\lambda)}+\sqrt{\left(\frac{30}{\frac{Q_{NACP}(d_2)}{Q_{NACP}(d_1)}\xi_1^2\,(4-\lambda)}+\frac{5}{(4-\lambda)}-1\right)^2+\frac{120}{\frac{Q_{NACP}(d_2)}{Q_{NACP}(d_1)}\xi_1^2\,(4-\lambda)}}}, \tag{5.3.12}$$

which can be solved numerically for the parameter ξ_1^2, and the general collection efficiency may then be determined according to (4.2.31).

The original expression for the general collection efficiency according to Seemann would be interesting to investigate for LICs, since it would likely be even more robust than the approximation derived in paper IV. However, this is not possible since the two-dose-rate method requires matched ratios of chamber readings, e.g. $Q_M(d_1)/Q_M(d_2)$ and $Q_{NACP}(d_1)/Q_{NACP}(d_2)$. As a

consequence, the final expression for the general collection efficiency used in the two-dose-rate method cannot be a polynomial of an order higher than one. This can be realized if the general collection efficiency according to Seemann is expressed according to the two-dose-rate methodology, which results in

$$
\frac{f(d_1)}{f(d_2)} = \frac{Q_M(d_1)}{Q_M(d_2)}\frac{Q_0(d_2)}{Q_0(d_1)} = \frac{1+\frac{1}{6}\frac{Q_0(d_2)}{Q_0(d_1)}\xi_1^2\left(1-\frac{4-\lambda}{10}\left(1-\frac{Q_M(d_1)}{Q_0(d_1)}\right)\right)^2}{1+\frac{1}{6}\xi_1^2\left(1-\frac{4-\lambda}{10}\left(1-\frac{Q_M(d_1)}{Q_0(d_1)}\right)\right)^2}. \tag{5.3.13}
$$

Here, the ratio $Q_M(d_1)/Q_0(d_1)$ is the very same quantity that the two-dose-rate method aims to determine, i.e. the general collection efficiency $\left(f(d_1)\right)$. Furthermore, this mixed ratio cannot be reformulated according to the two-dose-rate methodology using readings from a reference ionization chamber, i.e. $Q_0(d_i) = Q_{NACP}(d_i)$.

The separation of initial and general recombination in the two-dose-rate method was investigated in detail for continuous beams in paper IV. Here, the results by Mie (1904) were employed to qualitatively describe the distortion of the collecting electric field following ionization of the sensitive media. The fundament of the two-dose-rate method for continuous beams is a reformulation of the parameter $q_0(d_i)$, from the total amount of charge created per unit time and volume to the corresponding quantity escaping initial recombination. For this reformulation to be valid, it can be realized that initial recombination in a liquid must have a negligible influence on the distortion of the collecting electric field, and vice versa. To qualitatively illustrate the distorted collecting electric field in a PTW microLion LIC, the parameter $\sqrt{z}$ (4.2.19) has been determined using the manufacturer specifications of the measurement volume dimensions and liquid specific parameters according to the work by Johansson and Wickman (1997). The results from these calculations for general collection efficiencies between 70 and 99% are shown in figure 5.3.1 for a theoretical model of a microLion LIC containing isooctane and tetramethylsilane, respectively.

Isooctane − Distorted collecting electric field

Tetramethylsilane − Distorted collecting electric field
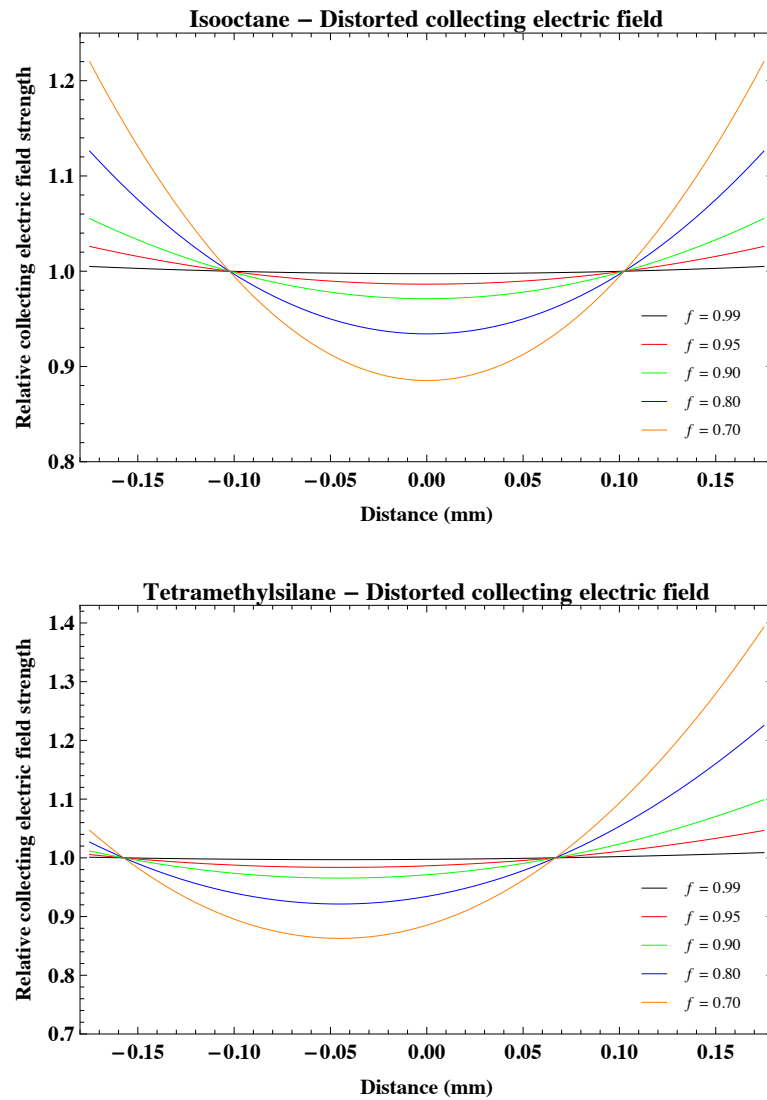
Figure 5.3.1. A qualitative description of the distorted collecting electric field according to the work by Mie (1904) for a PTW microLion LIC containing isooctane and tetramethylsilane, respectively, for general collection efficiencies between 70 and 99%.

In figure 5.3.1, the anode and cathode side in the qualitative model of the distorted collecting electric field in a microLion LIC are found at the left and right hand y-axis, respectively. Initial recombination has a dependence on the collecting electric field strength, which will be spatially distorted by the charge densities created by ionization, e.g. as described by the results from Mie (1904). The separation of initial and general recombination in the two-

dose-rate method will thus not be well explained by the cancellation of the escape probabilities from initial recombination at dose rates d_1 and d_2 employed in the work by Tölli *et al* (2010) and paper I. To examine the separation in detail, the amount of charge created per unit time and area escaping initial recombination $\left(J(d_i)\right)$ at a dose rate d_i can be expressed as

$$J(d_i) = \int_{-h/2}^{h/2} q_0(d_i) \, f_I\big(E(d_i, x)\big) \, dx, \qquad (5.3.14)$$

where $q_0(d_i)$ is the total amount of charge created per unit time and volume, and $f_I\big(E(d_i, x)\big)$ the escape probability from initial recombination for the local collecting electric field strength at x, and h the electrode separation. Given the formulation in (5.3.14), the separation of initial and general recombination in the two-dose-rate method can be expressed as

$$\frac{J(d_1)}{J(d_2)} = \frac{Q_0(d_1)}{Q_0(d_2)} = \frac{\int_{-h/2}^{h/2} q_0(d_1) \, f_I\big(E(d_1, x)\big) \, dx}{\int_{-h/2}^{h/2} q_0(d_2) \, f_I\big(E(d_2, x)\big) \, dx}. \qquad (5.3.15)$$

Assuming that the ionization of the sensitive media in a LIC is homogeneous, $q_0(d_i)$ can be taken out of the integrals in (5.3.15), which gives

$$\frac{Q_0(d_1)}{Q_0(d_2)} = \frac{q_0(d_1)}{q_0(d_2)} \frac{\frac{1}{h}\int_{-h/2}^{h/2} f_I\big(E(d_1, x)\big) \, dx}{\frac{1}{h}\int_{-h/2}^{h/2} f_I\big(E(d_2, x)\big) \, dx} = \frac{q_0(d_1)}{q_0(d_2)} \frac{\overline{f_I}\big(E(d_1)\big)}{\overline{f_I}\big(E(d_2)\big)}. \qquad (5.3.16)$$

Here, $\overline{f_I}\big(E(d_i)\big)$ represents the spatial average of the escape probability from initial recombination at a dose rate d_i. From (5.3.16) it was realized that the separation of initial and general recombination in the two-dose-rate method requires that $\overline{f_I}\big(E(d_1)\big) = \overline{f_I}\big(E(d_2)\big)$. It is thus not trivial to assume that the ratio of escape probabilities from initial recombination will cancel for a given pair of dose rates d_1 and d_2. Consequently, the separation of initial and general recombination has to be accepted as an approximation in the two-dose-rate methodology $\left(\overline{f_I}\big(E(d_1)\big) \approx \overline{f_I}\big(E(d_2)\big)\right)$. The viability of this approximation must be determined experimentally, since the two-dose-rate method does not employ any explicit modelling of initial recombination.

5.3.1. Analysis of the two-dose-rate method

The two-dose-rate method for pulsed beams, which was observed to achieve robust corrections for general recombination (Tölli *et al*, 2010), was compared to the three-voltage method in paper III. The results for the lowest and highest dose per pulse for LICs containing isooctane and

tetramethylsilane, respectively, are shown in figure 5.3.1.1. Furthermore, the general collection efficiencies according to the two-dose-rate method for pulsed beams are given in table 5.3.1.1 and 5.3.1.2 for isooctane and tetramethylsilane, respectively.
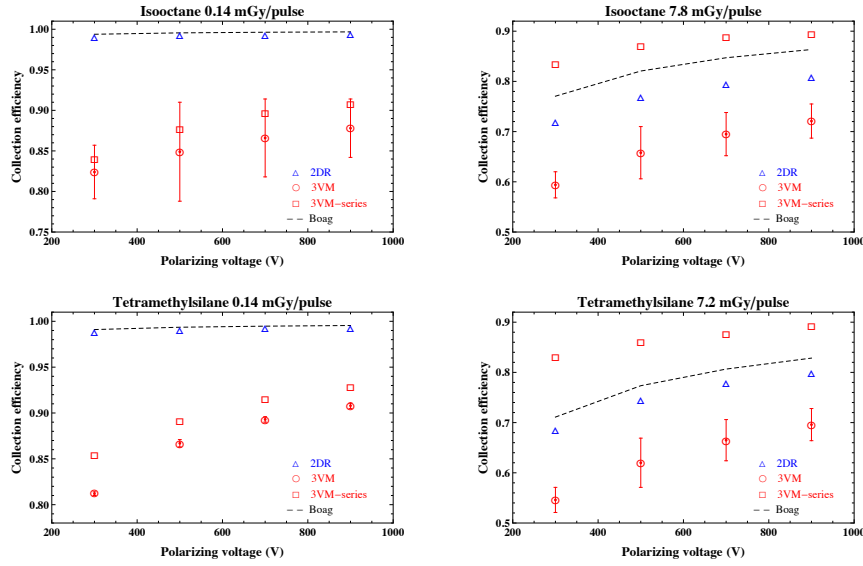
Figure 5.3.1.1. Examples of results from the comparison between the two-dose-rate (2DR) and three-voltage method (3VM) for microLion LICs containing isooctane and tetramethylsilane, respectively. Shown here are results for the lowest and highest dose per pulse, respectively, from the experiments involving pulsed beams of 20 MeV electrons. Also shown is the theoretical general collection efficiency according to Boag (1950), where the dashed line has been added to guide the eye of the reader.

In addition to the results from the two-dose-rate and three-voltage methods, figure 5.3.1.1 also display results from the series expansion approach to the three-voltage method (3VM-series) suggested by Pardo-Montero and Gómez (2009). As an illustration of a theoretical approach, direct calculation of the general collection efficiency for pulsed beams according to the work by Boag (1950) is also shown in figure 5.3.1.1.

Table 5.3.1.1. General collection efficiencies determined according to the two-dose-rate method for the microLion LIC containing isooctane for the experiments involving pulsed beams of 20 MeV electrons. Values in the parenthesis represent one relative standard deviation.

| Dose per pulse (mGy pulse^{-1})	300 V	500 V	700 V	900 V
0.14	0.991 (0.1)	0.993 (0.1)	0.993 (0.1)	0.994 (0.1)
0.28	0.984 (0.1)	0.987 (0.2)	0.989 (0.2)	0.989 (0.2)
0.43	0.975 (0.4)	0.980 (0.4)	0.982 (0.5)	0.983 (0.5)
0.57	0.969 (0.3)	0.975 (0.4)	0.977 (0.4)	0.979 (0.4)
0.78	0.957 (0.4)	0.966 (0.5)	0.970 (0.6)	0.972 (0.6)
1.2	0.939 (0.8)	0.950 (1.0)	0.955 (1.1)	0.958 (1.2)
2.6	0.870 (0.9)	0.894 (1.1)	0.905 (1.2)	0.910 (1.3)
4.2	0.818 (0.5)	0.852 (0.6)	0.869 (0.6)	0.879 (0.7)
5.7	0.776 (0.5)	0.818 (0.6)	0.838 (0.7)	0.850 (0.7)
7.8	0.720 (0.8)	0.769 (0.9)	0.795 (1.0)	0.810 (1.1)

Table 5.3.1.2. General collection efficiencies determined according to the two-dose-rate method for the microLion LIC containing tetramethylsilane for the experiments involving pulsed beams of 20 MeV electrons. Values in the parenthesis represent one relative standard deviation.

Dose per pulse (mGy pulse^{-1})	300 V	500 V	700 V	900 V
0.14	0.989 (0.1)	0.991 (0.1)	0.993 (0.1)	0.993 (0.1)
0.28	0.979 (0.2)	0.984 (0.2)	0.987 (0.2)	0.988 (0.2)
0.43	0.967 (0.4)	0.975 (0.4)	0.979 (0.3)	0.980 (0.5)
0.56	0.959 (0.4)	0.969 (0.3)	0.974 (0.2)	0.976 (0.4)
0.73	0.948 (0.4)	0.960 (0.4)	0.967 (0.3)	0.970 (0.4)
1.3	0.909 (1.2)	0.928 (1.2)	0.938 (1.3)	0.944 (1.5)
2.7	0.831 (0.2)	0.865 (0.2)	0.883 (0.1)	0.894 (0.3)
4.3	0.773 (0.7)	0.821 (0.8)	0.846 (0.8)	0.861 (0.9)
5.3	0.742 (0.7)	0.796 (0.8)	0.822 (0.8)	0.838 (0.9)
7.2	0.686 (0.7)	0.745 (0.8)	0.778 (0.8)	0.799 (0.9)

As shown in paper III, the two-dose-rate method is more robust than the three-voltage method. This can be observed when comparing the general collection efficiencies and the corresponding relative standard deviations for the two-dose-rate method (table 5.3.1.1 and 5.3.1.2) and the three-voltage method (table 5.2.1.3 and 5.2.1.4). The only instance where the three-voltage method for pulsed beams achieves results with reasonably small standard deviations is for the lowest dose per pulse (0.14 mGy pulse^{-1}) for the LIC containing tetramethylsilane. The results from the two-dose-rate method yields relative standard deviations predominantly smaller than 1%, when considering all possible combinations of LIC readings from the different dose per pulse settings employed in the experiments involving pulsed beams of 20 MeV electrons.

The two-dose-rate method for continuous beams based on the expression by Greening (1964) derived in paper I was also compared to the three-voltage method in paper III for experimental data from the experiments involving 120 kV x-rays. The results from the three-voltage method for continuous

beams appear to be better than for the case of pulsed beams, but the agreement to the more robust two-dose-rate method is still only within experimental uncertainties for very small general recombination losses (< 1%). Examples of the results from the respective methods for continuous beams are shown in figure 5.3.1.2.
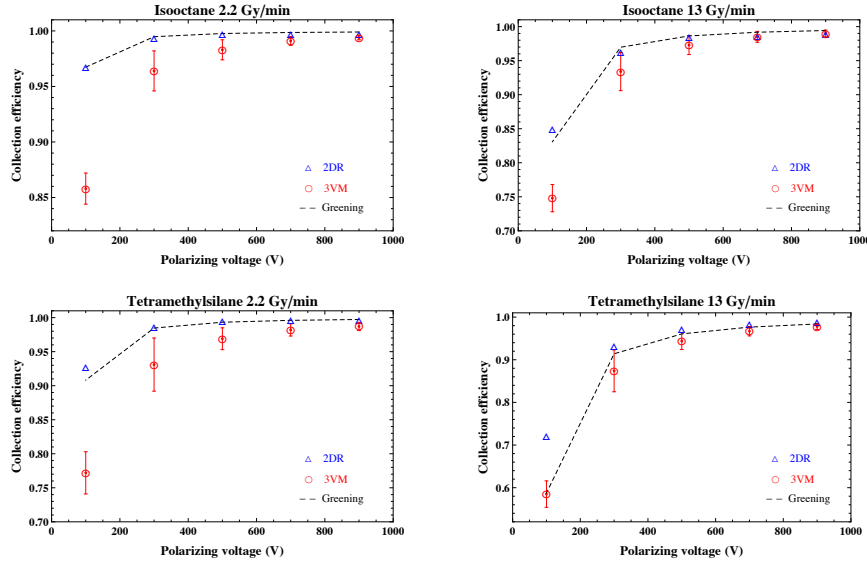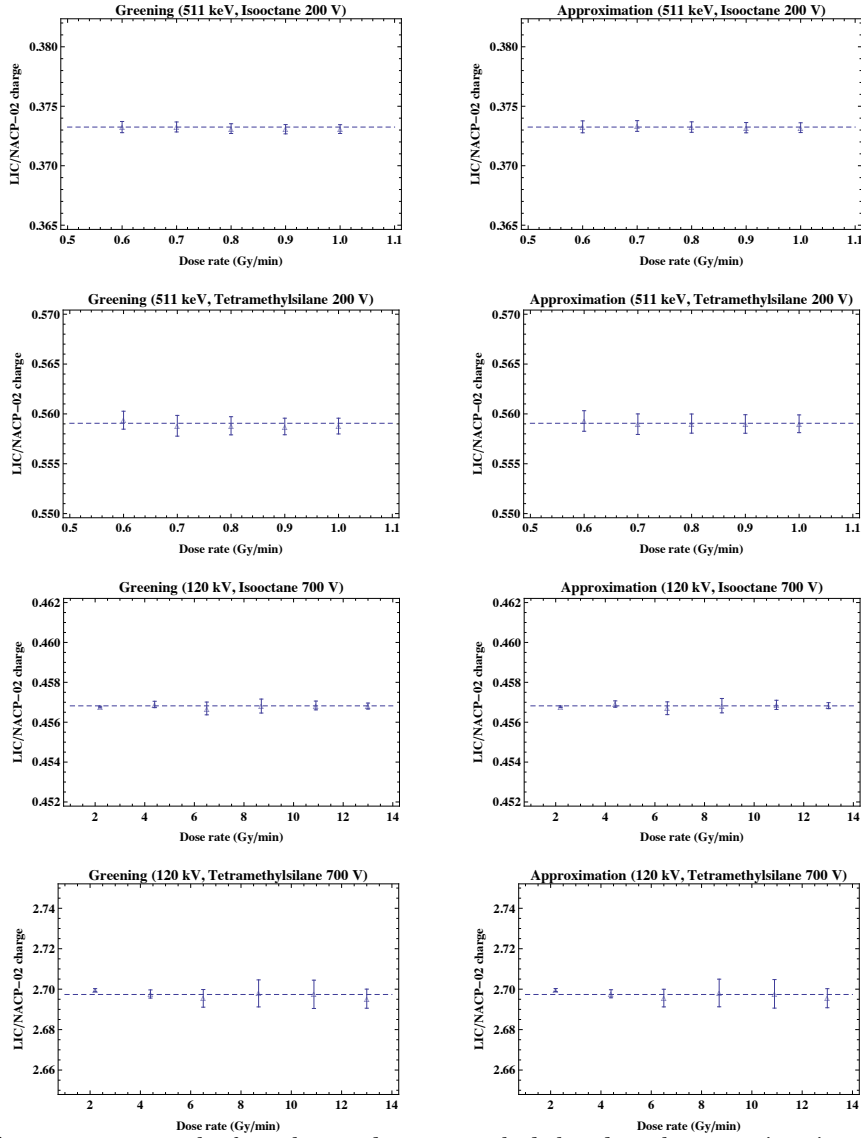

Figure 5.3.1.2. Examples of results from the comparison between the two-dose-rate (2DR) and three-voltage method (3VM) for microLion LICs containing isooctane and tetramethylsilane, respectively. Shown here are results for the lowest and highest dose rates employed in the experiments involving 120 kV x-rays. Also shown is the theoretical general collection efficiency according to Greening (1964), where the dashed line has been added to guide the eye of the reader.

Paper II included an application of the two-dose-rate method for continuous beams, based on the expression by Greening (1964), for 511 keV annihilation photons. Here, the range of validity for experimentally determined general collection efficiencies appeared to be greater for annihilation photons (> 70%) compared to 120 kV x-rays (> 90%). This was found by comparing the resulting corrected LIC to NACP-02 ratios from the respective experiments. It was discussed in paper II that this indicates that the separation of initial and general recombination in the two-dose-rate method may have dependence on the radiation quality.

In paper IV, a two-dose-rate method based on the new approximation (5.3.12) of the general collection efficiency according to Seemann (1912) was employed with experimental data from 120 kV x-rays and 511 keV annihilation photons. Furthermore, the results were compared to those from the original two-dose-rate method for the respective radiation qualities
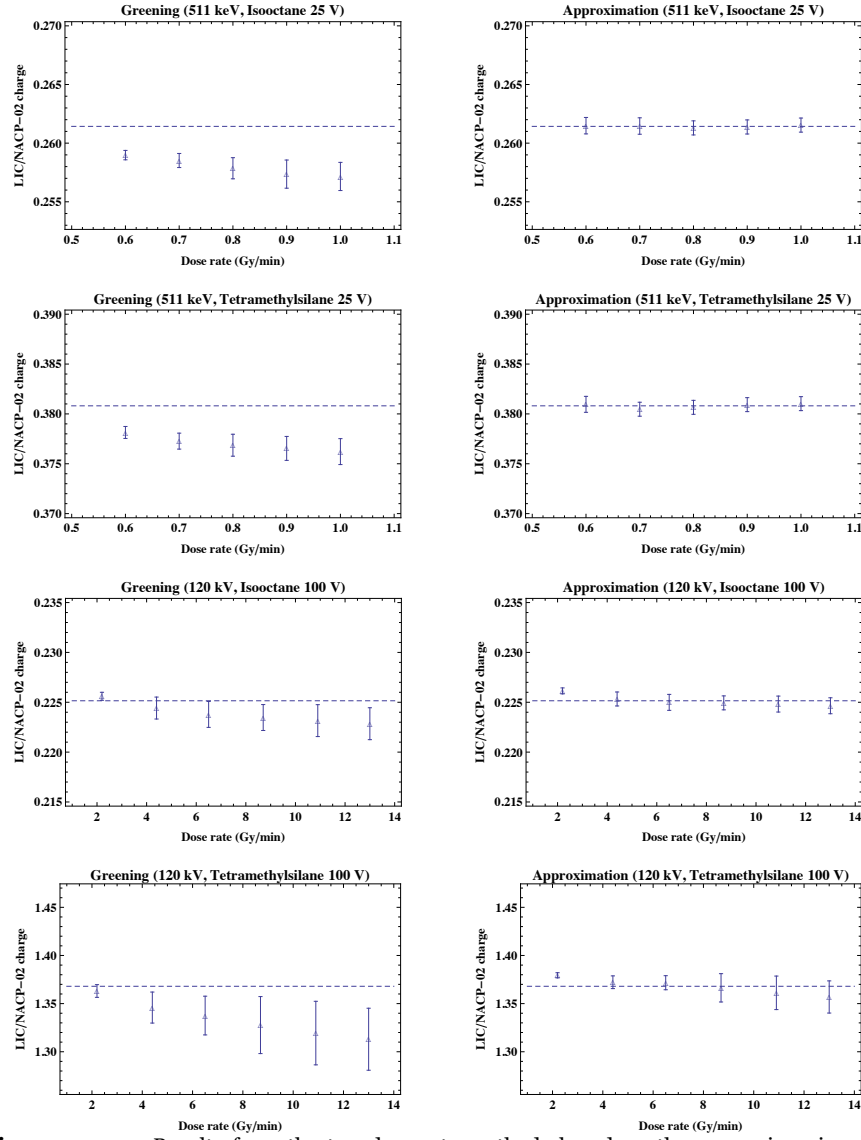
(paper I and II). A comparison of the results from the respective method is shown in figure 5.3.1.3 for microLion LICs containing isooctane and tetramethylsilane, respectively, for general collection efficiencies above 90%.

Figure 5.3.1.3. Results from the two-dose-rate methods based on the expression given by Greening (1964) and the approximation derived in paper IV for continuous beams of 120 kV x-rays and 511 keV annihilation photons. Shown here are results for microLion LICs containing isooctane and tetramethylsilane, respectively, for general collection efficiencies above 90%. The dashed line represents the mean corrected LIC to NACP-02 ratio according to the method based on the approximation derived in paper IV.

Furthermore, a comparison of the results from the respective method is shown in figure 5.3.1.4 for microLion LICs containing isooctane and tetramethylsilane, respectively, for general collection efficiencies below 90%.

Figure 5.3.1.4. Results from the two-dose-rate methods based on the expression given by Greening (1964) and the approximation derived in paper IV for continuous beams of 120 kV x-rays and 511 keV annihilation photons. Shown here are results for microLion LICs containing isooctane and tetramethylsilane, respectively, for general collection efficiencies below 90%. The dashed line represents the mean corrected LIC to NACP-02 ratio according to the method based on the approximation derived in paper IV.

As seen in the examples in figure 5.3.1.3, the results from the different two-dose-rate methods compared are very similar for general collection efficiencies above 90%. When comparing all results for $f > 0.9$, the maximum deviation between the results from the respective method is 0.1%. For general collection efficiencies below 90%, the method based on the approximation derived in paper IV achieves an improvement in the results for both 120 kV x-rays and annihilation photons, as seen in figure 5.3.1.4. This is theoretically reasonable given the robustness of the approximation derived in paper IV, as shown in figure 4.2.2. However, the signal to dose rate linearity in the corrected LIC to NACP-02 ratios is still questionable or poor for the microLion LICs containing isooctane and tetramethylsilane, respectively, for an applied voltage of 100 V ($f < 0.9$). The theoretical modelling of general recombination employed in the present work cannot be used to explain these results. As discussed in paper IV, it is likely that the condition for the separation of initial and general recombination $\left(\overline{f}_I(E(d_1)) \approx \overline{f}_I(E(d_2))\right)$ is violated for the lowest applied voltage for the experiments involving 120 kV x-rays. To illustrate this, a comparison of individual general collection efficiencies determined for a primary dose rate $\left(f(d_1)\right)$ as a function of LIC readings from a complementary dose rate (d_2) is shown in figure 5.3.1.5.
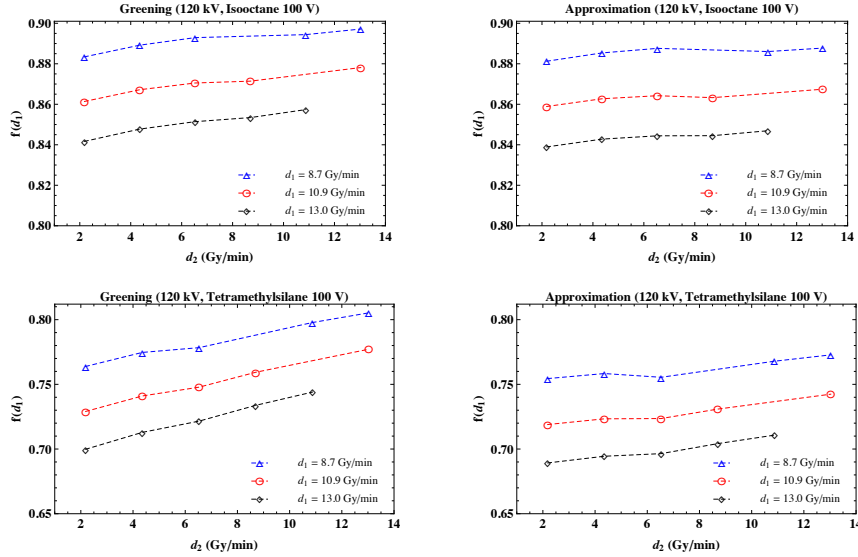
Figure 5.3.1.5. Examples of individual general collection efficiencies $f(d_1)$ as a function of LIC readings at a complementary dose rate d_2 according to the methods based on the expression given by Greening (1964) and the approximation derived in paper IV, respectively. The calculations are based on measurements from the experiments involving continuous beams of 120 kV x-rays. The dashed lines in each data series have been added to guide the eye of the reader.

The trend observed in the respective individual general collection efficiencies as a function of the complimentary dose rate in figure 5.3.1.5 can likely be attributed to an incomplete separation of initial and general recombination in the two-dose-rate method. If the general collection efficiency for a primary dose rate $\left(f(d_1)\right)$ is determined from combinations with LIC readings at dose rates d_2 and d_3, for which $\overline{f}_I\!\left(E(d_1)\right) < \overline{f}_I\!\left(E(d_2)\right) < \overline{f}_I\!\left(E(d_3)\right)$, a trend in the individual results will be observed similarly to those found in figure 5.3.1.5. Moreover, as seen in figure 5.3.1.5, there is a difference in the results for the LICs containing isooctane and tetramethylsilane, respectively. As discussed in paper IV, the separation of initial and general recombination in the two-dose-rate method is complicated by a radiation quality dependence of initial recombination, as well as differences in the initial recombination characteristics for different liquids.

The condition for initial recombination $\left(\overline{f}_I\!\left(E(d_1)\right) \approx \overline{f}_I\!\left(E(d_2)\right)\right)$ governing the separation of initial and general recombination in the two-dose-rate method is naturally not limited to the case of continuous beams. A similar trend as that shown in figure 5.3.1.5 for results from the two-dose-rate method for continuous beams can also be found for pulsed beams. This is illustrated in figure 5.3.1.6 for the experiments involving pulsed beams of 20 MeV electrons.
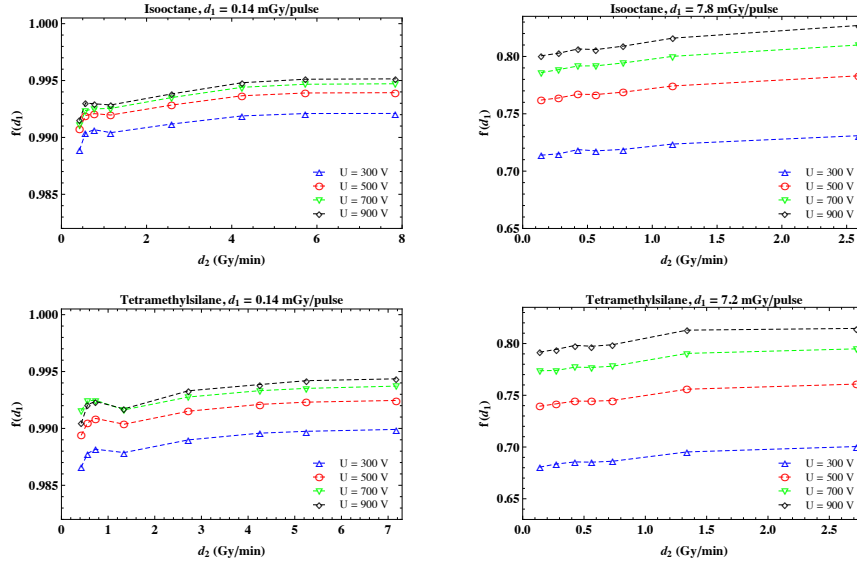
Figure 5.3.1.6. Examples of individual general collection efficiencies $f(d_1)$ as a function of LIC readings at a complementary dose rate d_2 according to the two-dose-rate method for pulsed beams (Tölli *et al*, 2010). The calculations are based on measurements from the experiments involving pulsed beams of 20 MeV electrons. The dashed lines in each data series have been added to guide the eye of the reader.

As seen in figure 5.3.1.6, the individual general collection efficiencies determined by the two-dose-rate method for pulsed beams display a clear trend with the complementary dose per pulse (d_2) for d_1 equal to 7.8 mGy pulse^{-1} and 7.2 mGy pulse^{-1} for isooctane and tetramethylsilane, respectively. Here, the difference between a general collection efficiency $\left(f(d_1)\right)$ determined from the lowest and highest complimentary dose rate (d_2) is between 2 and 3% for all investigated applied voltages to the LICs. For the lowest dose per pulse shown in figure 5.3.1.6, the difference between a general collection efficiency $\left(f(d_1)\right)$ determined from the lowest and highest complimentary dose rate (d_2) is at most 0.3%, which may be considered as within the experimental uncertainties. This indicates that the space charge effect influences the results from the two-dose-rate method for pulsed beams, i.e. causing a violation of the requirement $\overline{f_l}\left(E(d_1)\right) \approx \overline{f_l}\left(E(d_2)\right)$ for a high dose per pulse. As seen in figure 5.3.1.6, for the lowest dose per pulse (0.14 mGy pulse^{-1}), the general collection efficiency is very close to unity and the space charge effect is thus likely negligible. Unfortunately, the semi-empirical nature of the work by Boag (1950) prohibits an analysis of the space charge effect in pulsed beams similar to that done for continuous beams in the present work. It has been suggested that the space charge effect is small in liquids for a low or moderate dose per pulse (Gregg and Bakale, 1970). While this is a reasonable conclusion, it does not offer any help in a

theoretical analysis of the space charge effect in LICs irradiated by pulsed beams.

As discussed in paper II, it is interesting to compare the ratios of corrected LIC readings from the experiments involving 120 kV x-rays and 511 keV annihilation photons. The ratio of LIC readings corrected for general recombination according to the two-dose-rate method derived in paper IV Q_{TMS}/Q_{ISO} is 5.95 ± 0.11 for the experiments involving 120 kV x-rays, and the corresponding ratio is 1.49 ± 0.02 for the experiments involving annihilation photons. Here, the ratios have been taken pairwise per applied voltage for the respective experiments. The results for the lowest applied voltage (100 V) from the experiments involving 120 kV x-rays have been excluded here due to the problems with the separation of initial and general recombination, as previously discussed. From the Monte Carlo simulations of the experiments employed in paper II, the absorbed dose to the respective liquids per emitted photon (D_{liquid}) may be determined. It has thus been possible to estimate the absorbed dose ratio $(D_{TMS}/D_{ISO})_{511\,keV}$ to 0.98 ± 0.02. Corresponding Monte Carlo simulations have been performed for the experiments involving 120 kV x-rays in the work by Johansson *et al* (2013) for the microLion LIC containing isooctane. These Monte Carlo simulations have also been extended to the microLion LIC containing tetramethylsilane by the author (personal communication), and the ratio $(D_{TMS}/D_{ISO})_{120\,kV}$ has been determined to 3.29 ± 0.07. By employing the ratios of corrected charge and absorbed dose, a quantity proportional to the ratio of the free-ion yield (G_{fi}) in tetramethylsilane and isooctane can be determined. The resulting values of these ratios are 1.52 ± 0.04 and 1.81 ± 0.04 for 511 keV annihilation photons and 120 kV x-rays, respectively. As a comparison, Schmidt and Allen (1970) have reported values of the free-ion yield for tetramethylsilane and isooctane corresponding to a ratio $G_{fi}^{TMS}/G_{fi}^{ISO} = 2.2$. The corresponding values of free-ion yields reported by Jay-Gerin *et al* (1993) gives a ratio $G_{fi}^{TMS}/G_{fi}^{ISO} = 2.0$. The differences in initial recombination characteristics between isooctane and tetramethylsilane, indicated by the values of G_{fi} reported in the literature, can be used to explain the differences between these liquids observed in figure 5.3.1.5. The ratios of charge readings corrected for general recombination and normalized to the absorbed dose to the respective liquid indicates that there is a significant difference in the initial recombination characteristics for annihilation photons and 120 kV x-rays. The implicit radiation quality dependence of initial recombination may thus help to explain the differences found in the separation of initial and general recombination in the two-dose-rate method for the experiments involving annihilation photons and 120 kV x-rays.

6. Summary of papers

Short summaries of the papers in this thesis are given in the following subsections.

6.1. Paper I

Application of the two-dose-rate method for general recombination correction for liquid ionization chambers in continuous beams

Andersson J and Tölli H

Phys. Med. Biol. **56** (2011) 299-314

Aim: The development of an experimental method (the two-dose-rate method) for general recombination correction for liquid ionization chambers employed for measurements in continuous beams. The two-dose-rate method, which disassociates initial and general recombination, is based on a theoretical modelling of general recombination according to Greening's theory for general recombination in air-filled ionization chambers.

Methods: The two-dose-rate method for continuous beams based on the theory by Greening has been evaluated with experimental data from measurements with two liquid ionization chambers containing isooctane and tetramethylsilane, respectively, in continuous x-ray beams from a computed tomography unit. An x-ray tube potential of 120 kV was used in the experiments and the dose rates were varied between 2.2 and 13 Gy min^{-1}. The liquid ionization chambers were operated with applied voltages of 100, 300, 500, 700 and 900 V, for both liquids investigated.

Results: The veracity of the resulting corrections for general recombination was evaluated by the signal to dose rate linearity in the corrected liquid ionization chamber readings. The results were in excellent agreement with the reference air-filled ionization chamber employed in the experiments for general collection efficiencies over 90 %, for both liquids.

Conclusions: The two-dose-rate method for general recombination correction for liquid ionization chambers in continuous beams based on Greening's theory can achieve robust corrections for general recombination losses less than 10 %.

6.2. Paper II

On the property of measurements with the PTW microLion chamber in continuous beams

Andersson J, Johansson E and Tölli H

Med. Phys. **39** (2012) 4775-87

Aim: An investigation of the performance of the PTW microLion liquid ionization chamber with respect to general recombination losses and perturbations from ambient electric fields at various dose rates from continuous beams of 511 keV annihilation photons.

Methods: Measurements were performed with two PTW microLion liquid ionization chambers containing isooctane and tetramethylsilane, respectively, in continuous beams of 511 keV annihilation photons from the decay of the radioactive isotope Fluorine-18 (^{18}F). The maximum dose rate employed in the experiments was approximately 1 Gy min^{-1}, as determined by Monte Carlo simulations, and the liquid ionization chambers were operated with applied voltages between 25 and 500 V. The general recombination losses in the liquid ionization chambers were determined by the two-dose-rate method for continuous based on the theory by Greening.

Results: The corrections for general recombination according to the two-dose-rate method achieved a good signal to dose rate linearity in the liquid ionization chamber readings for general collection efficiencies above 70 %. Perturbations from ambient electric fields were found in the liquid ionization chamber readings at lower dose rates. Experimental data from dose rates below approximately 0.2 Gy min^{-1} were therefore excluded from the investigation of general recombination losses. The perturbations were observed to increase in strength with an increase in the applied voltage.

Conclusions: By comparing results from the two-dose-rate method for 120 kV x-rays and 511 keV annihilation photons, it can be concluded that the method achieves comparable corrected ionization currents for low and medium energy photon beams. The valid range of general collection efficiencies is experimentally observed to be different for low and medium energy photons. The PTW microLion chamber is sensitive to ambient electric fields, which can be a limiting factor in practical application of this dosimeter.

6.3. Paper III

A comparison of different experimental methods for general recombination correction for liquid ionization chambers

Andersson J, Kaiser F-J, Gómez F, Jäkel O, Pardo-Montero J and Tölli H

Phys. Med. Biol. **57** (2012) 7161-75

Aim: A comparison of existing methods for general recombination correction for liquid ionization chambers for pulsed and continuous beams.

Methods: Experimental data from measurements with PTW microLion chambers containing isooctane and tetramethylsilane, respectively, for continuous beams (120 kV x-rays) and pulsed beams (20 MeV electrons) has been employed with the two-dose-rate and the three-voltage method, respectively. The two-dose-rate method achieves correction for general recombination losses by a disassociation of initial and general recombination, while the three-voltage method explicitly models both initial and general recombination.

Results: The results were evaluated by the signal to dose rate (or dose per pulse) linearity in the corrected liquid ionization chamber readings. The three-voltage method fails to achieve accurate corrections for general recombination for both continuous and pulsed beams in many instances, predominantly for low applied voltages and dose rates. For the case of continuous beams, and applied voltages in the range recommended by the manufacturer, the agreement between the methods is generally within the experimental uncertainties. This corresponds to general collection efficiencies above 99 %. For the case of pulsed beams, the results from the three-voltage method are generally poor.

Conclusions: The two-dose-rate method is presently the most robust experimental method available for general recombination correction for liquid ionization chambers. The inaccuracy of the three-voltage method can partially be traced to numerical problems, which makes the method sensitive to small variations in the experimental data. The results also suggest that the modelling of initial recombination employed in the three-voltage method may contribute to the problems found.

6.4. Paper IV

A study of recombination losses in liquid ionization chambers

Andersson J and Tölli H

Submitted to Phys. Med. Biol.

Aim: A study of the applicability of theory for general recombination derived for gases to liquid ionization chambers.

Methods: A new and robust relation to describe general recombination has been derived from existing theory for gases to evaluate the process of general recombination in liquids. Experimental data from 120 kV x-rays and 511 keV annihilation photons was evaluated by the two-dose-rate method to disassociate initial and general recombination and the theory by Greening, as well as the more robust expression derived in the present work.

Results: The results indicate that the process of general recombination is similar in liquids and gases, since a stronger modelling of general recombination for gases also improves the results for liquids. The disassociation of initial and general recombination in the two-dose-rate method is complicated by that initial recombination has a spatial dependence on the collecting electric field, which in turn is used to derive and express the general collection efficiency. The dependency of initial recombination on the radiation quality, as well as the type of liquid employed as the sensitive media in a liquid ionization chamber has been found to further complicate corrections for general recombination losses at low applied voltages and general collection efficiencies.

Conclusions: A dedicated theory that combines initial and general recombination to express the conduction of electricity through an ionized liquid is needed to further improve the knowledge of liquid ionization chambers.

7. Discussion and conclusions

The adoption of liquid ionization chambers (LICs) in radiation dosimetry has primarily been prevented by the lack of a robust experimental method to achieve corrections for general recombination. The theories derived to describe general recombination in gases (Boag 1950, Greening 1964) have previously been applied directly for rough approximations of the general recombination losses in order to distinguish possible applications for LICs. In the present work, the developed two-dose-rate method has been investigated and proven to be a robust experimental tool for general recombination correction for LICs (paper I-IV). It is thus now possible to consider the use of LICs according to existing formalisms for clinical radiation dosimetry in therapeutic and diagnostic applications, e.g. TRS-398 (IAEA, 2000) and TRS-457 (IAEA, 2007).

Due to the presence of both initial and general recombination in ionized liquids, the two-dose-rate method is based on a mathematical separation of initial and general recombination. As shown in paper IV, this separation is not trivial. By the qualitative use of the work by Mie (1904) applied to liquids, it has been realized that the collecting electric field in a LIC is distorted following the ionization of the liquid employed as the sensitive media. The distortion of the collecting electric field increases with increasing dose rate, i.e. with decreasing general collection efficiency. Meanwhile, initial recombination, which is always present in an ionized liquid, depends on the collecting electric field strength in each point between the electrodes. These two recombination processes are thus interdependent. While the escape probability from initial recombination determines the amount of charge available to undergo general recombination, the amount of general recombination will influence the escape probability from initial recombination through the distorted collecting electric field. Furthermore, the veracity of the separation of initial and general recombination in the two-dose-rate method will depend on the type of liquid used as the sensitive media as well as the radiation quality employed, due to the implicit radiation quality dependence of initial recombination.

The three-voltage method for general correction for LICs proposed by Pardo-Montero and Gómez (2009) has been shown to be inferior to the two-dose-rate method in paper III. Severe issues have been identified with the robustness of the three-voltage method, manifested in numerical problems and a strong dependence on the set of applied voltages employed for the LICs. The three-voltage method employs an explicit modelling of initial recombination according to Mozumder's treatment (1974a) of the Onsager

theory (1938), which by itself should be reasonable for a LIC containing isooctane (Pardo *et al*, 2004). However, by mathematically combining theoretical modelling of both initial and general recombination it is likely that the interdependence between these processes, through the distorted collecting electric field, is not properly taken into account. This interpretation is supported by the dependence on the applied voltages chosen in the results from the three-voltage method.

While paper IV elaborates on the separation of initial and general recombination mathematically and experimentally for the case of continuous beams, the two-dose-rate method for pulsed beams (Tölli *et al*, 2010) is also affected by the space charge effect, as discussed in the present work. However, a comparable analysis for pulsed beams is not easily achieved due the semi-empirical nature of the derivation of the expression for general recombination in pulsed beams according to the work by Boag (1950). In fact, in the derivation of the general collection efficiency for pulsed beams the space charge effect is assumed to be negligible. The applicability of this approach is not easily interpreted for LICs.

A complication with all work on the property on recombination in LICs is the lack of dedicated theory to describe both initial and general recombination in liquids. As a consequence, the present work consistently makes use of theories derived for gases in an approximate manner to describe and interpret ion recombination in liquids. As shown in paper IV, this approach has merit since liquids mimic the theoretical behaviour expected from gases according to the strength of the modelling for general recombination. However, it must be recognized that dedicated theories for both initial and general recombination in liquids are needed to further the understanding of recombination mechanisms in LICs.

Beyond the methodology and theory investigated in the present work, there are also practical issues to consider regarding the use of LICs in radiation dosimetry. As observed in paper II, the commercially available microLion LIC (PTW, Germany) has an intrinsic sensitivity to ambient electric fields, which may perturb measurement results. The sensitivity to perturbations from ambient electric fields may be due to the lack of a guard electrode in this chamber type, as well as a possible insufficient shielding of the chamber body. The suspected weakness of the microLion chamber construction should be further investigated and solved. Furthermore, the use of LICs for measurements in pulsed beams is not trivial given the high pulse repetition frequencies used in modern linear accelerators. The signal response of liquids commonly used in LICs is too slow for these pulse repetition frequencies due to low ion mobilities, which will result in pulse overlap in

the measurement signal. This will in turn definitely invalidate the work by Boag (1950) as a possible source for an adequate modelling of general recombination for LICs, since it requires well separated measurement signal pulses.

In conclusion, from the methodology developed in the present work it is possible to consider adoption of LICs in radiation dosimetry and thus take advantage of what this technology has to offer. The primary strength of LICs is a high spatial measurement capability coupled with that the liquids employed as the sensitive media have energy absorption properties that are similar to water. The two-dose-rate method is also well suited for considerations of new LIC designs, primarily to decide measurement volume dimensions for a given application, but also for studies on finding optimal liquids for a given radiation quality or a pulse rate repetition frequency. In addition to applications for radiation dosimetry, the present work also offers new possibilities to study intrinsic characteristics of ionized liquids. Here, initial recombination is key process connected to the conduction of electricity through liquids.

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