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DIPLOMARBEIT

Methods for increasing the specific activity of ^{51}Cr to produce enriched radioactive chromium(III)-tris(2,2,6,6-tetramethyl-3,5-heptanedionate)

zur Erlangung des akademischen Grades

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Abstract

This Master's thesis describes the preparation of high specific activity ^{51}Cr labeled chromium(III)-tris(2,2,6,6-tetramethyl-3,5-heptanedionate) ($\text{Cr}(\text{tmhd})_3$). An introduction to nuclear physics, neutron activation and gamma ray spectroscopy is provided, followed by a discussion of the chemical effects of nuclear transformations (Szilard-Chalmers effect), which allow chemical separation (enrichment) of neutron-induced ^{51}Cr . ^{51}Cr is produced by neutron irradiation of target materials (ammonium chromate and $\text{Cr}(\text{tmhd})_3$), which are applied as ^{51}Cr sources to radiolabel $\text{Cr}(\text{tmhd})_3$. The targets are compared with each other regarding their suitability for radiolabeling of $\text{Cr}(\text{tmhd})_3$. Enrichment of ^{51}Cr from both targets by chemical means is assessed and liquid-liquid extraction (ammonium chromate) and chromatography on silica gel ($\text{Cr}(\text{tmhd})_3$) are applied. A comprehensive overview of the methods used for the application of enriched ^{51}Cr in a radiosynthesis of $\text{Cr}(\text{tmhd})_3$ is provided.

Kurzfassung

Diese Masterarbeit beschreibt die Herstellung von ^{51}Cr radiomarkiertem Chrom(III)-tris(2,2,6,6-tetramethyl-3,5-heptandionat) ($\text{Cr}(\text{tmhd})_3$) mit hoher spezifischer Aktivität. Die Arbeit beginnt mit einer Einführung in die Kernphysik, die Neutronenaktivierung und Gammaspetrokopie, gefolgt von einer Diskussion der chemischen Effekte von Kernumwandlungen (Szilard-Chalmers Effekt), der chemische Separation (Anreicherung) von neutroneninduziertem ^{51}Cr ermöglicht. Durch Neutronenbestrahlung von Targetmaterialien (Ammoniumchromat und $\text{Cr}(\text{tmhd})_3$) erzeugtes ^{51}Cr wird als Quelle für die Radiomarkierung von $\text{Cr}(\text{tmhd})_3$ verwendet, wobei die Materialien in Hinblick auf diese Anwendung miteinander verglichen werden. Es wird die Anreicherung von ^{51}Cr durch Flüssig-Flüssig-Extraktion (Ammoniumchromat) und durch Chromatographie mit Kieselgel ($\text{Cr}(\text{tmhd})_3$) diskutiert. Die Arbeit gibt einen umfassenden Überblick über die Anwendung von angereichertem ^{51}Cr in einer Radiosynthese von $\text{Cr}(\text{tmhd})_3$.

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1 Motivation

Radio tracers are useful tools for measurement of physical properties or quantities, since radioactivity can be measured very precisely. It offers the additional advantage that, depending on the system, it can often be measured non-destructively. Another advantage is that spatially resolved measurements are easy to realize. In addition, different isotopes of an element behave chemically almost identically. However, slight differences do exist, for example, in all physically dominated processes, in which the mass of individual atoms plays a role, a small change in the mass of isotopes may be important. In most chemical processes it does not matter whether an isotope is radioactive or not, so the use of radio-labeled chemicals offers a wide range of applications.

The hypothesis tested in this study is the chemical separation (enrichment) of neutron-induced ^{51}Cr from neutron-irradiated bulk Cr-containing target materials (Szilard-Chalmers processes) may be exploited to generate high specific activity chromium(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate) ($\text{Cr}(\text{tmhd})_3$) for tracer applications.

There were three main aims in this work: Firstly, demonstration of chemical incorporation of neutron-induced ^{51}Cr from bulk irradiated Cr-containing target materials into a $\text{Cr}(\text{tmhd})_3$ synthesis. Secondly, optimization of chemical processes for isotopic enrichment of ^{51}Cr from neutron-irradiated ammonium chromate and $\text{Cr}(\text{tmhd})_3$. Two different concepts are described, one being chemically separation from irradiated ammonium chromate using liquid-liquid extraction and the other being separation from irradiated $\text{Cr}(\text{tmhd})_3$ by chromatography on silica gel. The advantages and disadvantages of these two methods are compared and it will be explained why liquid-liquid extraction was preferred. And thirdly, the chemically separated neutron-induced ^{51}Cr is applied in a radiosynthesis of $\text{Cr}(\text{tmhd})_3$ to maximize the ^{51}Cr specific activity in a hydrocarbon soluble radio tracer.



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2 Background and general methods

In the following chapter, a brief overview of the basics of nuclear physics is first given. The most important terms for the following Master's thesis are introduced and neutron activation and measurement methods as central components are explained. The focus is then placed on the Szilard-Chalmers effect, which is the basis of the experimental work. Starting with the explanation of the effect, some chemical terms and experimental working steps that were necessary to carry out the chemical experiments are explained here.

2.1 Nuclear physics

2.1.1 Binding energy

The binding energy of a nucleus is the energy required to break a nucleus into its constituent parts. The same amount of energy is released when the nucleons form a nucleus. This energy comes from the strong interaction between quarks, which are the constituents of neutrons and protons. The following describes a semi empirical model for binding energy, the liquid-drop model, in which the nucleus is described like an incompressible liquid droplet. The Bethe-Weizsäcker formula is quite inaccurate for small nuclei with a nucleon number below 30, but for nuclei above that the deviation is only less than 1 % [1].

$$E_B = a_V A - a_S A^{\frac{2}{3}} - a_C \frac{Z(Z-1)}{A^{\frac{1}{3}}} - a_A \frac{(N-Z)^2}{A} + a_P \delta(N, Z) A^{-\frac{1}{2}} \quad (2.1)$$

The binding energy of a nucleus (with nuclear charge number Z , neutron number N and nucleon number A) is composed of the following parts: The volume term (proportional to A) explains that each nucleon contributes to the binding energy due to its strong interaction with surrounding nucleons. The surface term (proportional to $A^{\frac{2}{3}}$) accounts for the fact that nucleons are surrounded by fewer neighbors at the surface than in the interior. The Coulomb term (proportional to $Z(Z-1)A^{-\frac{1}{3}}$) accounts for the reduction in binding energy due to the

Coulomb repulsion of the protons. This fraction becomes more significant the larger a nucleus is and explains why nuclei with an atomic number greater than 82 (lead) are not stable. The symmetry term comes from Fermi statistics and decreases the binding energy the larger the difference between neutron and proton number. Lastly, the pairing term must be added, which takes into account that nuclei with odd neutron or proton numbers are more unstable than nuclei with even numbers. This can explain the shell model with the spin of the nucleons. The values for the parameters a are determined experimentally and may vary slightly depending on the mass range for which the formula was optimized.

For a detailed description of the strong interaction on particle physics level is referred to the literature, e.g. [2].

2.1.2 Reactor physics

Neutron activation by neutron irradiation requires a neutron source which are usually nuclear reactors. Although there are also some sources based on spontaneous fission or, for example, (α, n) reactions, the great advantage of reactors is their much larger neutron flux [3]. Spallation sources can be used as an alternative to research reactors. Although they require an accelerator and are therefore more expensive to build, they have advantages in terms of radioactive waste and nowadays also reach a large flux of $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ [4]. In a nuclear reactor, (typically) ^{235}U is fissioned after capture of thermal neutrons, releasing neutrons again. In the fission process, a uranium nucleus captures a neutron and enters a highly excited intermediate state that is not stable and decays into two fragments and normally two or three neutrons. A typical example is the following reaction: $^{235}_{92}\text{U} + {}^1_0\text{n} \longrightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3 {}^1_0\text{n}$.

Only in a fraction of the cases in the promille range three fragments are formed [5]. During fission, energy is released due to the difference in mass defect. For nuclei with more than 200 nucleons, the binding energy per nucleon is about 1 MeV larger than for the fragments with usually 90 to 140 nucleons. Therefore, on average, about 200 MeV is released per fission. Most of this is converted to heat as the kinetic energy of the fission products. Only a small part, the energy of the antineutrinos and a part of the gamma radiation, is lost [6]. The energy of the resulting neutrons follows a Maxwell distribution, with the average energy being about two MeV. The neutrons are distinguished on the basis of their energy, which is connected by the formula

$$\langle E \rangle = \frac{3}{2} k_B T \quad (2.2)$$

with the temperature, between cold and ultracold neutrons (energy less than 25 meV and temperature below 200 K), thermal neutrons (energy about 25 to

100 meV, temperature 200 K), epithermal neutrons (up to 1 eV, 8000 K) medium-fast (up to 500 keV, 4×10^9 K) and fast neutrons (over this value) [6].

Since the cross section for neutron capture, apart from a few resonance maxima in the upper energy range, is orders of magnitude higher for thermal neutrons than for fast neutrons, the resulting fast neutrons have to be moderated, i.e. decelerated, in order to be available for a new fission of ^{235}U and to maintain a chain reaction. The moderator is usually water, other possibilities are heavy water (consisting of deuterium instead of hydrogen) or carbon. Depending on the size and purpose of the reactor, there are a variety of designs that use different moderators and cooling systems. For the different reactor types and their advantages and disadvantages in application, it is referred to further literature.

The TRIGA (Training, Research, Isotopes, General Atomic) reactor at the Atomic Institute of the Technische Universität Wien is a research reactor with a power up to 250 kW in continuous operation and several hundred MW in pulsed operation. At the Atomic Institute, the TRIGA reactor is available for isotope production, experiments with neutrons and radiochemistry, and for educational purposes in reactor physics. The reactor is a swimming pool reactor, the reactor core is located in a water pool several meters deep, which serves as cooling and shielding of the radiation. The moderator used is uranium zirconium hydride (UZrH) [7]. The TRIGA type of reactor was developed by Edward Teller in the 1950s as a teaching reactor, intended to be so safe that it "could be given to a bunch of high school children to play with, without any fear that they would get hurt." [8] cited from [9]. This inherent safety is generated by a very strong negative temperature coefficient of reactivity. This means that when the power is increased and the temperature increases along with it, the moderation capability decreases sharply, leaving fewer thermal neutrons available for further fission processes and interrupting the chain reaction.

2.1.3 Neutron activation

In the present work, the reactor is available as a thermal neutron source for neutron activation by neutron irradiation. In this process, singular nuclei absorb an additional neutron. After the absorption of an additional neutron, the nucleus is in a highly excited state. During the transition to the ground state, prompt γ photons are emitted. These photons are called prompt because they are released within fractions of a second. Some nuclei (most notably the isotopes ^1H , ^{12}C , ^{14}N , ^{16}O and ^{28}Si , which occur naturally) are stable even with an extra neutron. However, many nuclides are radioactive with an additional neutron. The resulting unstable nuclei decay with a specific half-life to an often excited daughter nucleus that emits the excess energy in the form of discrete γ radiation

(delayed γ photons). The nuclear transformation that happens here is a weak interaction process and is called β decay. In β^- decay, a neutron converts to a proton, producing an extra electron (the β particle) and an antineutrino. β^+ decay occurs in nuclei that have too few neutrons to be stable. Here, a proton converts to a neutron and a positron, and a neutrino is released. Competing with this process there is electron capture. Here an electron of the innermost shell is captured by the nucleus and a proton transforms into a neutron and neutrino. An example of electron capture is the decay of the chromium isotope ^{51}Cr . At the elementary particle level, there is an interaction between the up and down quarks of protons and neutrons with W and Z bosons, which results in a transformation of the quarks. These processes are the only physical interactions in which a transformation of elementary particles occurs. For a detailed description of the weak interaction on particle physics level is referred to the literature, e.g. [2].

2.1.4 Activation equation

The activity $A(t)$ of a radioactive substance is the number of decays per time and is expressed in Becquerel. One Becquerel means one decay per second. Mathematically, the following equation links the activity to the number of nuclei N via the decay constant λ , which is related to the half-life τ via $\lambda = \frac{\ln 2}{\tau}$:

$$A(t) = -\frac{dN}{dt} = \lambda N(t) \quad (2.3)$$

Here $N(t)$ is the (time-dependent) number of radioactive nuclei.

If additional radioactive nuclei are produced by neutron irradiation of N^* (inactive) atoms, this can be calculated with the following equation:

$$\frac{dN}{dt} = -\lambda N(t) + N^* \Phi \sigma \quad (2.4)$$

with the neutron flux density Φ and the cross section for neutron capture σ .

Solving the differential equation with the initial condition $N(0) = 0$ (this means there are no radioactive nuclei at the beginning) yields:

$$A(t) = \Phi \sigma N^* (1 - e^{-\lambda t}) \quad (2.5)$$

The activity increases with time and more and more radioactive nuclei are produced by the irradiation. Strictly speaking, one would have to consider, of course, that the amount of inactive nuclei becomes less by the irradiation at the same time and thus N^* also changes. However, since the number of

activated nuclei is often several orders of magnitudes smaller than N^* , the time-dependence of N^* can usually be neglected. The last term in the bracket of Equation 2.5 indicates that radioactive nuclei already formed during activation decay again. Since more nuclei decay when the number of radioactive nuclei is higher, the increase of activity becomes flatter with time and the activity converges to the saturation activity A_S for large times. After seven half-lives, about 99% of the saturation activity is reached, thus the activity hardly changes with further irradiation time.

$$A_S = \Phi\sigma N^* \quad (2.6)$$

2.1.5 Neutron activation analysis

The delayed γ photons are delayed by milliseconds to billions of years compared to the prompt γ radiation, depending on the half-life, and are isotope-specific. Therefore, they can be measured in the detector and used for elemental analysis. This analysis is called neutron activation analysis (NAA).

NAA is very well suited for the analysis of ceramics (and other archaeologically important substances, for example pumice), because the main components of the samples cannot be activated by neutrons (subsection 2.1.3). Thus, there is less background radiation and better measurement results for trace elements and rare earth elements. For example, if the sample contains sodium, individual ^{23}Na atoms in the reactor are activated during irradiation and decay into ^{24}Mg with a half-life of about 15 hours (β^-), emitting γ photons with energies of 2.76 MeV and 1.38 MeV. $^{23}_{11}\text{Na} + {}^1_0\text{n} \longrightarrow {}^{24}_{11}\text{Na} + \gamma_{\text{prompt}} \longrightarrow {}^{24}_{12}\text{Mg} + \text{e}^- + \bar{\nu}_e + 2\gamma$. The existence of these two γ lines indicates that the sample contains sodium and the intensity of the lines gives information about the amount.

2.2 Gamma-ray spectroscopy

Gamma spectroscopy is the measurement of gamma radiation from a radioactive source. In the next chapter the origin, the interaction and the detection of gamma radiation is explained.

2.2.1 Origin of gamma radiation

Just like the discrete energy levels of the electrons in an atom, the nuclei themselves have discrete energy levels, but they are several orders of magnitude further apart than those of the electrons. During nuclear transitions, radiation is emitted with the same principles, which is called gamma radiation because

of its large energy and its origin in the nucleus. In radioactive decays, the nucleus usually remains in a highly excited state after the transition and emits this excess energy with a specific half-life and energy depending on the nuclide. Frequently, several photons are also emitted in succession, and the nucleus does not fall back to the ground state directly, but in a number of steps. The measurement of this radiation gives precise information about the composition of a radioactive sample [10].

2.2.2 Interaction of photons with matter

Photons interact with matter much less strongly than α and β particles of the same energy due to their lack of mass and charge, and therefore have a greater depth of penetration. The interaction and absorption of photons in matter occurs mainly via the following three effects: Photoelectric effect, Compton effect and pair formation. Which of these processes is dominant depends largely on the energy of the photons. At low energies the photoelectric effect dominates, but decreases strongly at very large energies. Pair formation is possible only at photon energies larger than 1.022 MeV and becomes more dominant beyond that. The cross section for the Compton effect is relatively constant over a wide energy range and dominant in an intermediate energy range (about 300 keV to 3000 keV), below which the photoelectric effect dominates and above which pair formation dominates [11].

Photoelectric effect

A photon can release all its energy at once to an electron, creating an electron-ion pair and the free electron receives the photon energy as kinetic energy minus the electron binding energy. For the mathematical explanation (Equation 2.7) of this phenomenon in 1905, Einstein received the Nobel Prize in 1921 [12].

$$E = h\nu - W \quad (2.7)$$

Here E is the kinetic energy of the electron, $h\nu$ the energy of the photon and W the binding energy of the electron in the atom. The electron produces secondary ionization in matter just like any other β particle. The photoelectric effect affects electrons from an inner shell (e.g. K or L) and subsequently soft X-rays are produced when the gap is filled by outer electrons [13].

Compton effect

In the Compton effect, which like the photoelectric effect is an indication of the particle nature of photons, a photon transfers part of its energy to a quasi-free

electron (in an outer shell) and is scattered by an angle as in a collision of two balls. The photon continues to propagate with reduced energy (i.e. longer wavelength) until it has given up its remaining energy by further Compton scattering, the photoelectric effect or pair formation. The energy transfer from photon to electron and thus the wavelength shift of the photon is only a function of the scattering angle [14]:

$$\lambda' - \lambda = \frac{h}{m_e c} (1 - \cos \theta) = \frac{2h}{m_e c} \sin^2 \frac{\theta}{2} \quad (2.8)$$

Here λ' and λ are the wavelengths of the scattered and incident photon, h is Planck's constant, m_e is the rest mass of the electron, c is the speed of light, and θ is the scattering angle of the photon.

Pair formation

Pair formation is based on the energy-mass equivalence ($E = mc^2$). The photon energy is transformed into new matter, here necessarily always matter and antimatter are created in equal parts. Since the rest energy of all elementary particles except the electron is orders of magnitude higher than the energy of a γ photon released in radioactive decays, only electrons and positrons are created during pair formation. The minimum energy required for this is twice the rest energy of the electron $m_e = 511 \text{ keV}$, i.e. 1.022 MeV . The excess energy of the photon is distributed as kinetic energy between the electron and the positron. For reasons of conservation of momentum, pair formation is possible only in the electromagnetic field of an atomic nucleus, which can take over part of the momentum. The created electron behaves exactly the same as any other electron in matter, i.e. mostly via ionization of atoms and bremsstrahlung. The positron almost immediately annihilates with another electron to two photons with the respective rest energy of an electron 511 keV [13].

2.2.3 Types of detectors

One of the oldest variants of a measurement of ionizing radiation is that by means of a scintillator. In the earliest version, a zinc sulfide screen uses luminescence to trigger flashes of light from the high-energy photons, which can be counted. Modern detectors usually use salts (e.g. sodium iodide) or organic liquids in which the sample can be dissolved. This is followed by a photomultiplier, which uses the photoelectric effect to convert and amplify the very weak flashes of light into a measurable electron current, the amplitude of which depends on the energy of the incident radiation.

Another way of measuring radiation is the counting tube. Here, a cylindrical metal tube, with the outer wall being the cathode, is filled with a gas and a thin wire is run as the anode in the center of the cylinder. If ionizing radiation is incident, then free electrons and ions are produced in the gas as the name implies. The amount of DC voltage applied between the cathode and anode has a significant effect on the operation of the counting tube. At very low voltage, some of the electrons recombine on their way to the anode, therefore no specific information is obtained. If a voltage of the order 100 V is applied, all the electrons created reach the anode before they recombine (ionization chamber). Since the number of electrons depends on the energy of the incident radiation, the current pulse is proportional to it. At higher voltage, the electrons reach such high velocities that they ionize more atoms in the gas by impact ionization. Each electron is thus amplified and the resulting current pulse is still proportional to the incoming radiation energy, but is now more easily measurable (proportional band). Proportional counters are often used in hand-foot monitors in radiation protection areas. At even higher voltages, incident ionizing radiation triggers a self-sustained gas discharge; all the gas in the counting tube ignites regardless of the type and energy of the incident radiation. A counting tube used in this way is called a Geiger-Müller counter and is suitable for detecting radiation with very high sensitivity.

The most accurate detectors for gamma radiation are semiconductor detectors. In principle, their operation is the same as that of a classical ionization chamber, which must meet three characteristics: all the energy of the ionizing radiation must be deposited in the detector. All the electric charge generated must be collected and contribute to the pulse. No electric charges must be generated unless ionizing radiation is incident. A semiconductor detector fulfills all these three conditions [13].

2.2.4 The semiconductor detector: operation and signal generation

A semiconductor detector is essentially a p-i-n diode (made of germanium or silicon) operated in the reverse direction. The intrinsic region serves as the detection volume; within it, incident ionizing radiation generates electron-hole pairs. These are drawn off by the electric field to the p or n contacts, resulting in a current pulse. Since this pulse may have variations in shape and temporal extent, the intensity is not an indicator of incident energy. The integral over the pulse, on the other hand, yields a voltage proportional to the incident energy [15]. The signal is sent to an analog-to-digital converter and a multichannel analyzer, which plots the pulses by height in a histogram. Thus, a spectrum is

produced showing the number of pulses plotted against pulse height [13].

The main differences between a Ge and a Si detector are mainly based on the size of the band gap, the atomic number, and the resistivity of the material. A Ge detector has a much higher (thermal) leakage current due to its smaller band gap and therefore should be cooled with liquid nitrogen to suppress it. Therefore, it must be operated under vacuum and has an inlet window, making it less suitable for detecting α and β radiation.

In subsection 2.2.2, the interactions of photons with matter were explained. If a photon deposits its entire energy in the detector material, then the process contributes to the full-energy peak. Therefore, a material with the highest possible photoelectric cross section is advantageous for detector efficiency. Since the cross section increases strongly with the nuclear charge number, a Ge detector has a much higher efficiency than a Si detector.

Another major advantage of Ge detectors is the possibility to produce a single crystal of several centimeters thickness with a large purity. These detectors are called high-purity Ge (HPGe) detectors. The larger the extent of the depletion region, the greater the probability of a γ beam interacting with matter in the detector. Since the energy required to create an electron-hole pair in a Ge detector is very low compared to other materials, a lot more electron-hole pairs are generated per event and therefore the energy resolution is much better than for other detector materials.

2.2.5 Experimental method

For Gamma Spectrometry a High Purity Germanium (HPGe) detector (1.8 keV resolution at the 1332 keV ^{60}Co peak, 50.1% relative efficiency) connected to a Loss Free Counting System was used. Unless otherwise stated, the samples were measured in a reproducible geometry (C15 geometry, 15 mL sample solution in a 40 mL polypropylene container (Fisher Scientific 15468804, in the following called "Rotkappchen"). In general the solvent of the samples was ethyl acetate ($\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$ or short EtOAc). The measurement time was in general 5 minutes. The Genie 2000 Basic Spectroscopy Software version 3.4 from Canberra (RRID:SCR_021933) was used for the evaluation of the ^{51}Cr peaks at 320 keV. Count rates were decay-corrected for comparison.

2.3 Exploiting chemical effects of nuclear transformation

2.3.1 Szilard-Chalmers Effect

The Szilard-Chalmers effect was discovered in 1934 by Leó Szilárd and Thomas A. Chalmers. After the capture of thermal neutrons, the nucleus is in a highly excited state and releases this energy by emitting one or more prompt γ photons. The energies here are on the order of many hundreds of keV to a few MeV. As a result, the nucleus experiences a recoil of about 10 eV to 100 eV, which in most cases breaks chemical bonds (order of magnitude eV) [16]. The freed nuclei can now return to their bonding or they can form other bonds. In suitable chemical environments and with certain elements, the newly formed species can be chemically separated from the original irradiated compound, even though they are isotopes of the same element. Szilárd and Chalmers discovered this process after irradiating ethyl iodide. They were able to precipitate the activated iodine, which was no longer bound to ethane, with silver and extract it with water [17]. A detailed account of the experiment and the historical events prior to it can be found in [13]. Using the Szilard Chalmers effect, a high specific activity can be generated because the radioactive isotopes can be separated from the inactive ones in a chemical way. Examples from research in recent years can be found in [18][19][20][21][22].

The binding energy of the captured neutron in the activation of ^{50}Cr is 9.26 MeV [23]. This excess energy is released by two or more γ photons, making the recoil large enough to destroy the bond between Cr and O in $\text{Cr}(\text{tmhd})_3$, which have a mean bond dissociation energy 2.2 eV [24].

2.3.2 Chromatography

Chromatography is a chemical process for separating mixtures of substances. The name comes from the Greek $\chi\rho\acute{\omega}\mu\alpha$ for "color" and $\gamma\rho\acute{\alpha}\phi\epsilon\iota\nu$ for "write" because the Russian botanist Tswett, who first described the process in 1906, isolated dyes from each other [25]. It is based on the different interactions of substances with a mobile and a stationary phase. In chromatography, a mobile phase moves through a stationary phase on a mixture of substances. The individual substances within this mixture interact with both phases and are bound to the stationary phase for a certain time or run together with the mobile phase. The exchange between them occurs by diffusion. The different substances vary in the time they are on average in each of the phases. Due to the flow of the mobile phase, the difference in time results in a difference in speed

and thus in a separation. Chromatography is used, for example, in the analysis and in the purification of substances. Depending on the use of the phases, chromatography is further divided into sub-areas. In the following, thin layer and column chromatography are explained in more detail. For other methods and further information, please refer to the literature [26].

Thin layer chromatography

Thin layer chromatography is a chemical process for the qualitative separation of substance mixtures. The great advantage is the fast and simple feasibility with simultaneously high information gain and low substance quantities. A thin layer of a fine-grained (and usually) polar material (mostly silica gel) is used as the stationary phase. A mixture of a non-polar solvent (for example, hexane) and a low polar solvent (for example, ethyl acetate) is usually used as the eluent. The mixing ratio then determines the polarity of the eluent.

The dissolved sample is applied to the starting line of a thin layer plate using a capillary. The sample spot should be kept as small as possible so that the eluent passes through the entire starting spot at the same time, if possible. The plate is then placed in a (closed) chamber whose atmosphere is saturated with the solvent system. The mobile phase migrates upward through the thin film plate by capillary forces and transports the substances to different extents, depending on their polarity. Before the eluent front reaches the end of the plate, the plate is removed from the chamber and dried. This prevents the substances from moving further. The different substances are visible as dots or spots on the thin layer plate, depending on the substance with the naked eye, under UV light or only after treatment with suitable reagents [26].

Column chromatography

In column chromatography, a long glass tube is packed with the stationary phase (usually fine silica gel) together with the eluent. A layer of sand may be added to the top and bottom to protect the stationary phase. Similar to thin-layer chromatography, a mixture of polar and nonpolar solvent is most often used as the mobile phase so that polarity can be controlled by the composition. The sample solution is applied to the top of the column and slowly carried down through the column. The sample is (ideally) separated into the respective substances based on their different adsorption capabilities, which arrive at the end of the column with a time delay. This allows the different fractions to be collected.

In contrast to thin layer chromatography, it is possible to change the solvent during the experiment. For example, eluent gradients can be used where the

polarity is slowly increased so that a faster separation is obtained. The disadvantage of column chromatography is the relatively high effort in the execution or the relatively high consumption of chemicals, because the diameter of the column must be large enough so that the starting zone is not too large and the column must be long enough so that a reasonable separation takes place. Therefore, the amount of solvents used is relatively high [26].

2.3.3 Recrystallization

Recrystallization is a chemical process for the purification of substances and is based on the different solubility of substances. If a contaminated substance is dissolved in saturation, insoluble impurities can first be filtered off. Other impurities can be removed in the following way. If the saturation limit of the substances that are dissolved is slowly exceeded, these substances will crystallize out again. The principle behind purification is the substance to be purified is dissolved closer to the saturation limit than all the impurities. Therefore, the purified substance crystallizes out first. In most cases, the saturation limit is shifted by changing the temperature. For most substances, solubility is better in hot solutions than in cold ones. Thus, a hot saturated solution is cooled slowly, so that the cooling causes the saturation limit to drop and the product to recrystallize [27].

Another method of manipulating the saturation limit is to change the solvent by diffusion. If an open vial containing a saturated solution is placed in a closed chamber containing a different solvent, molecules of one solvent diffuse into the other and vice versa over an extended period of time. However, this changes the saturation limit of the new solvent mixture and the substance that is in saturation crystallizes out. This method was preferred in the following work when working with radioactive substances.

A disadvantage of recrystallization is that a relatively large amount of substance is lost for the advantage of greater purity of a substance.

3 ^{51}Cr labeled $\text{Cr}(\text{tmhd})_3$

3.1 Introduction

This chapter describes the chemical incorporation of neutron-induced ^{51}Cr from irradiated bulk Cr-containing target materials into the synthesis of $\text{Cr}(\text{tmhd})_3$. The aim of this work was to produce ^{51}Cr radiolabeled $\text{Cr}(\text{tmhd})_3$. At first sight, a simple possibility would be to irradiate the $\text{Cr}(\text{tmhd})_3$ itself with thermal neutrons so that some ^{50}Cr atoms are activated. However, a large part of the ^{51}Cr is removed from the $\text{Cr}(\text{tmhd})_3$ on irradiation (see subsection 2.3.1) and is subsequently present in a different, unknown chemical form [18]. Thus, to obtain the ^{51}Cr radiolabeled $\text{Cr}(\text{tmhd})_3$, syntheses of $\text{Cr}(\text{tmhd})_3$ were carried out, with additional irradiated Cr added. For this added Cr, two possible substances were tested as irradiation targets: ammonium chromate and $\text{Cr}(\text{tmhd})_3$. The target is first irradiated with neutrons in the reactor and then added to a $\text{Cr}(\text{tmhd})_3$ synthesis. Subsequently, incorporation of the added ^{51}Cr into the $\text{Cr}(\text{tmhd})_3$ and the effects of additional sources of Cr on the synthesis of $\text{Cr}(\text{tmhd})_3$ were investigated. For this purpose, the synthetic yields are compared with the inactive synthesis and the amount of ^{51}Cr present as $\text{Cr}(\text{tmhd})_3$ after the synthesis was investigated. Both irradiation targets are compared and the differences are described. As a preliminary experiment, an inactive synthesis and the subsequent purification steps are explained. Afterwards, the syntheses with additional active ^{51}Cr spikes are discussed.

3.2 Experimental methods

3.2.1 $\text{Cr}(\text{tmhd})_3$ from $\text{Cr}(\text{NO}_3)_3$

Description of synthesis of $\text{Cr}(\text{tmhd})_3$ from $\text{Cr}(\text{NO}_3)_3$

The procedure is based on [28], with some adaptations [29] (using 1:3 stoichiometry and avoiding sublimation for purification). The aim is the synthesis of about 5 g of $\text{Cr}(\text{tmhd})_3$.

20.4336 g (0.340 220 mol) of urea ($\text{CO}(\text{NH}_2)_2$) from the ATI storage were weighed

into a beaker. 4.5026 g (11.252 mmol) of chromium(III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) from Riedel-de Haën AG (now Honeywell Riedel-de-Haën) were weighed into a small plastic pan. Approximately 7 mL of 2,2,6,6-tetramethyl-3,5-heptanedione (TMHD) (98%) from Sigma-Aldrich were withdrawn with a 10 mL syringe and weighed. As the syringe is relatively inaccurate, the TMHD was weighed instead of measuring the volume. The density of TMHD is 0.883 g/mL, therefore 6.11 g (33.2 mmol) corresponds to 6.92 mL. About 65 mL of ethanol (EtOH) were poured into a measuring cylinder and diluted to 90 mL total volume with water. The weighed portion of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, the mixture of ethanol and water and the urea were filled to a 250 mL round-bottomed flask through a plastic funnel. The chromium nitrate dissolved well, urea not as well.

The round bottom flask containing the mixture was attached to a reflux condenser and heated on a 120 °C oil bath. A magnetic stirrer (400 rpm) was used to ensure constant mixing of the solution. The apparatus is shown in Figure 3.1. Upon reaching reflux, the now homogeneous mixture had turned emerald green. The weighed amount of TMHD (6.1478 g, 33.36 mmol) was then added drop wise over one minute. The mixture was boiled for 24 h on the 120 °C oil bath, with the reflux condenser ensuring that no solvent was lost. During this time the color of the solution changed from green to a dark purple. The next day, solid material and lilac crystals (the product) had precipitated. After 24 h, heating was discontinued and the mixture cooled to room temperature over a period of two hours. Subsequently, 100 mL of H_2O were added to ensure complete precipitation of the product. It was then vacuum filtered (800 mbar) using a Büchner funnel and a Büchner flask. The precipitate was washed with about 100 mL of H_2O . The filter cake was collected on a watch glass and left to dry in a desiccator, charged with potassium hydroxide at about 500 mbar for two days. The (raw) dry cake weighed 7.07 g.

Removal of EtOAc insoluble impurities

The dry powder (7.07 g of inactive $\text{Cr}(\text{tmhd})_3$) was dissolved in about 50 mL of ethyl acetate (EtOAc) and vacuum filtered (900 mbar). A large amount of lilac powder remained in the filter. Therefore, more solvent was used and the filter was changed after half of filtering. The solution was then dried on a rotary evaporator. Dried powder stuck to the sides of the flask and seemed to be wet with solvent. Therefore, the procedure was repeated. Then, the powder was left in the desiccator for three days. The dry filter cake was scratched from the flask and weighed (6.1242 g).

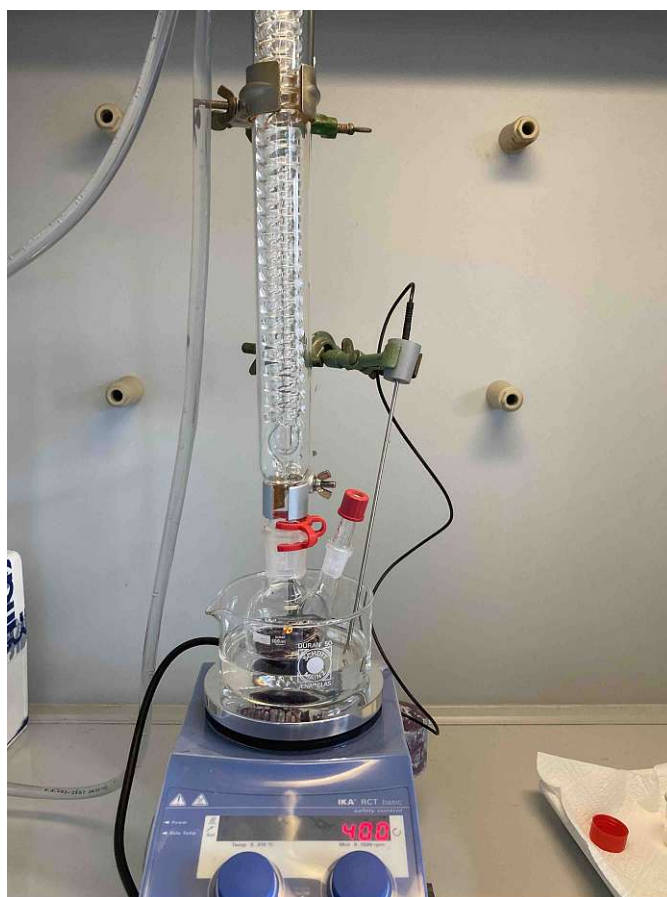


Figure 3.1: Apparatus for the synthesis of $\text{Cr}(\text{tmhd})_3$: a two-necked round-bottom flask with a reflux condenser, an oil bath, a lab jack and a magnetic stirrer.

Chromatography on silica gel

A mixture of 95% hexane (C_6H_{14}) and 5% ethyl acetate was prepared as the eluent for column chromatography. To do this, 190 mL of hexane was measured in a graduated cylinder, 10 mL of ethyl acetate was pipetted into an Erlenmeyer flask using a piston-stroke pipette, and then the hexane was added and the mixture homogenized. An aliquot of $Cr(tmhd)_3$ in powder form (697.1 mg) was dissolved at a concentration of about 100 mg/mL in the mobile phase. The resulting solution had a deep purple color.

Three beakers were prepared for the different fractions to be collected and tared. A slurry of 40 mL of silica gel and about 40 mL of the mobile phase was prepared by stirring in a beaker with a glass rod. The column was prepared with about 1 cm of sand, a few cm solvent, then the silica gel was added and more solvent was poured into the column. After a minute the silica gel settled (about 10 cm height) and 1 cm sand was added. The solvent was eluted until the surface of the silica gel was nearly exposed (fraction 1). The dissolved sample was then loaded onto the column with a glass pipette, then the sample beaker was washed out twice with 1 mL of solvent each time. Solvent was eluted until the surface of the silica gel was nearly exposed (fraction 1), and then additional solvent was added. The lilac solution was collected as fraction 2 and the remainder as fraction 3. A thin green layer remained on the surface of the silica gel. The weighed amount of purified product in fraction 2 after evaporation was 641.6 mg.

Recrystallization by cooling of a saturated EtOH solution

For further purification, a recrystallization with ethanol was carried out. In contrast to the later experiments with active material, in which the saturation limit is influenced by diffusion, a classical recrystallization with slow cooling of a saturated solution was utilized. Initially, about 20 mL ethanol was heated to boiling on a water bath. Then the dried $Cr(tmhd)_3$ sample from the above experiment (641.6 mg) was dissolved in it and filtered through a paper filter into an Erlenmayer flask. About 5 mL ethanol was used for rinsing. The filtration was intended to separate the insoluble foreign substances. The filter showed a slight green tint after filtration. Now the solution was boiled at about 82 °C until the liquid was reduced to ~10 mL. At this point, the hot plate was switched off and the flask was wrapped in aluminium foil so that further cooling would take place as slowly as possible (one day).

3.2.2 Cr(tmhd)₃ from Cr(NO₃)₃ spiked with neutron-irradiated Cr(tmhd)₃

The synthesis of unlabeled Cr(tmhd)₃ described above (see section 3.2.1) was scaled down to 500 mg (1/10 scale) and ⁵¹Cr in the form of irradiated Cr(tmhd)₃ was added at the beginning of the synthesis.

34.9 mg (0.0580 mmol) Cr(tmhd)₃ were irradiated for approximately 14 h¹ at a neutron flux density of about $1.7 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ in one of the five dry irradiation channel positions of the TRIGA Mark II reactor at the TRIGA Center Atominsti-tut in Vienna. After decaying (90 h), the irradiated sample was unpacked and dissolved in 7.5 mL ethanol. To speed the dissolution process an ultrasonic bath was used. Portions of urea (1.9953 g, 33.222 mmol), Cr(NO₃)₃·9H₂O (0.4504 g, 1.126 mmol) and the 2.5 mL H₂O were added to a 100 mL round bottomed flask. 6.5 mL (5.1426 g) of the irradiated sample dissolved in ethanol was withdrawn and added to the round-bottomed flask. The remainder (diluted to 15 mL) was set aside for gamma spectroscopic measurement (see subsection 2.2.5, using ethanol as solvent instead of the standard procedure). The resulting mixture was heated to reflux on a 120 °C oil bath during which time, the mixture turned a deep green color and TMHD (0.5309 g, 2.881 mmol) was added drop wise over half a minute. After 24 hours at reflux, the color of the mixture had changed to dark lilac Figure 3.2.

After cooling, in contrast to the inactive synthesis, no filtration was performed to avoid the handling of dry, radioactive powders. Initially, 10 mL of water H₂O was added to allow the product to precipitate completely. However, to separate the product formed from the remainder of the reaction mixture, extraction with chloroform (CHCl₃) was performed. Cr(tmhd)₃ is soluble in chloroform, which does not mix with the water-ethanol mixture and sinks due to its greater density. 20 mL of chloroform was added and the mixture was mixed with the magnetic stirrer so that as much as possible of the Cr(tmhd)₃ was dissolved from the walls of the flask in the chloroform. Then the chloroform that separated from the water could be extracted with a syringe into a beaker. The remaining water ethanol mixture was collected separately in a "Rotkappchen" and counted on the gamma spectrometer (see subsection 2.2.5, but with different amount of solvent). 20 mL of acetone ((CH₃)₂CO) was used to rinse the flask and also collected in a "Rotkappchen". The chloroform containing the ⁵¹Cr labeled Cr(tmhd)₃ was left for 2 days to dry. The dried powder was weighed (490.9 mg).

¹2 x 7 h with a 17 h break in between two consecutive reactor operation days.

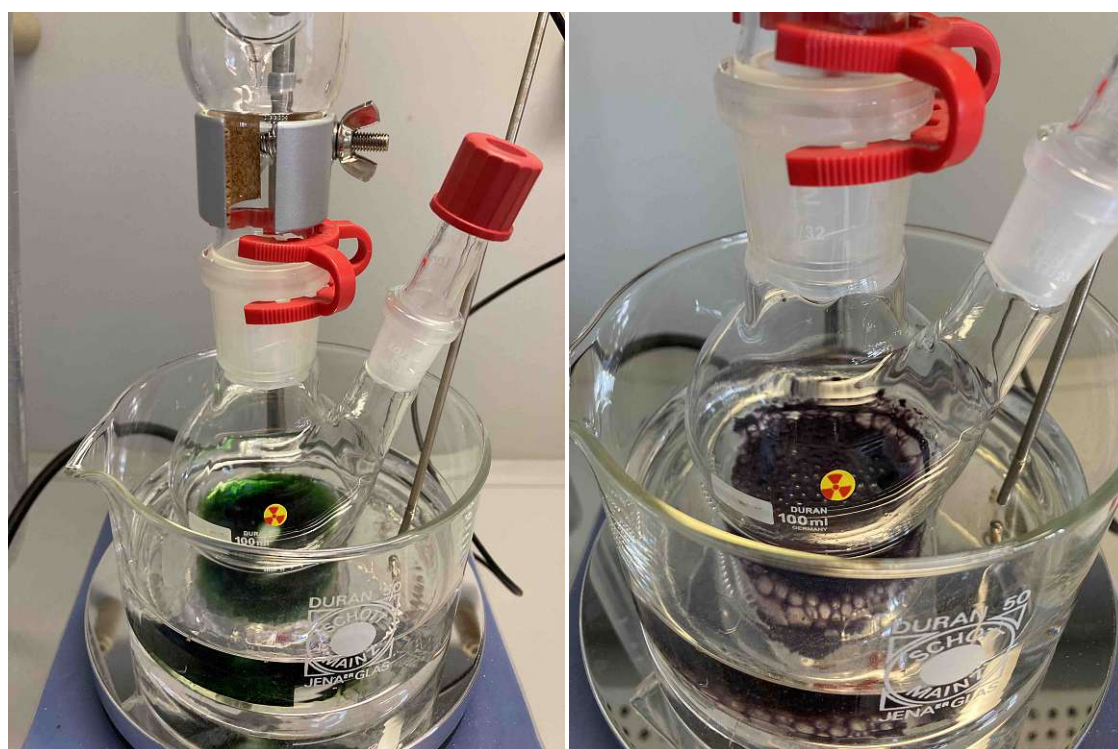


Figure 3.2: The color of the mixture to begin (green) and at the end (lilac) of a $\text{Cr}(\text{tmhd})_3$ synthesis can be seen.

Chromatography on silica gel

The material collected was subjected to a column chromatographic separation as described above (section 3.2.1). The $\text{Cr}(\text{tmhd})_3$ in powder form (490.9 mg) was dissolved to a concentration of about 100 mg/mL in the mobile phase. The resulting solution had a deep purple color.

Three beakers were prepared for the different fractions to be collected and tared. A slurry of 40 mL of Silica gel and about 40 mL of the mobile phase was prepared by stirring in a beaker with a glass rod. The column was prepared with about 1 cm of sand, a few cm solvent, then the silica gel was added and more solvent was poured into the column. After a minute the silica gel settled (about 10 cm height) and 1 cm sand was added. The solvent was eluted until the surface of the silica gel was nearly exposed (fraction 1). The dissolved sample was then loaded onto the column with a glass pipette, then the sample beaker was washed out twice with 1 mL of solvent each time. Solvent was eluted until the surface of the silica gel was nearly exposed (fraction 1), and then additional solvent was added. The lilac solution was collected as fraction 2 and the remainder as fraction 3.

Several areas of a slight greenish coloring were apparent during the chromatographic separation (see Figure 3.3). On top of the column some green crystals could be seen. A small fraction flowed with the mobile phase directly in front of the lilac phase and another fraction remained on top of the silica gel. The amount of purified product collected in fraction 2 was 337.0 mg.

Recrystallization by diffusion

In contrast to the recrystallization as a purification step after the inactive synthesis (see section 3.2.1), this step actually was not used as a purification method, but as a means to show that the ^{51}Cr distributes as the mass does.

Approximately 70 mg of substance was used for recrystallization. The purified $\text{Cr}(\text{tmhd})_3$ (337.0 mg) was dissolved in 15 ml EtOAc. 3.0 mL was taken with a pipette and left to dry, and then weighed (68.2 mg). Then the sample was dissolved in 15 mL EtOH, and the process was accelerated by an ultrasonic bath. To remove the green impurities that are not soluble in ethanol, the solution was filtered and then collected in a small glass vial (20 mL size). Three drops of EtOH were used to flush the filter and the sample vial. The filter was slightly greenish and was stored separately in a 90 mL polypropylene container (Semadeni 8905, in the following called "Gelbkäppchen"). For recrystallization, a "Gelbkäppchen" was filled with 30 mL H_2O , the glass vial was placed inside open, and then the "Gelbkäppchen" was sealed and allowed to stand for several days. During this time, purple crystals were formed.

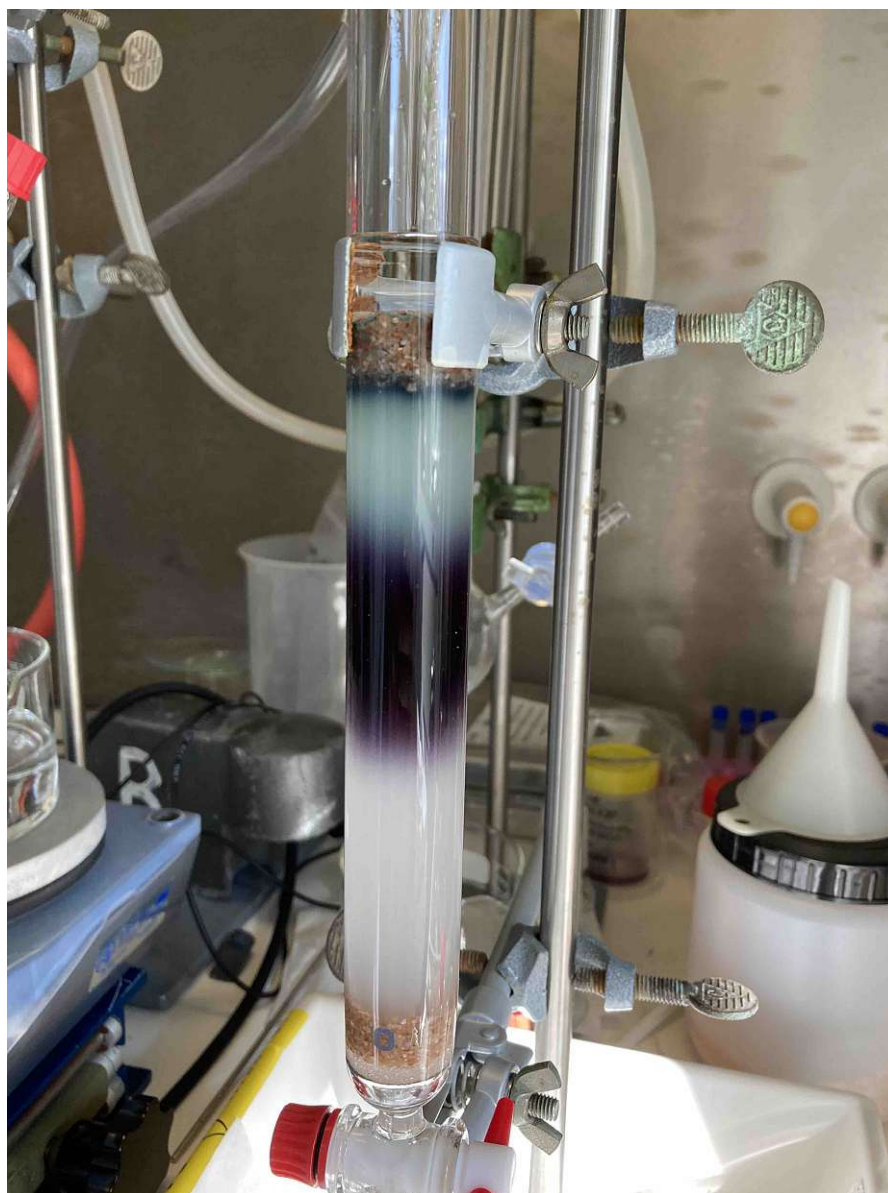


Figure 3.3: Here the chromatography column can be seen: the two layers of sand at the bottom and top, the silica gel in between (white), $\text{Cr}(\text{tmhd})_3$ (lilac), impurities that get stuck just below the sand at the beginning of the column (dark green) and impurities that travel a little slower than the product (light green).

After six days, the liquid fraction was withdrawn with a syringe and the resulting crystals were carefully washed with ethanol cooled in an ice bath, once with 1.5 mL and then with another 1 mL. The wash solutions were collected in a "Rotkäppchen". Then the crystals were transferred to a second "Rotkäppchen" with lukewarm ethanol. Both fractions were weighed after evaporation and then counted on the gamma spectrometer (see subsection 2.2.5). The recrystallized fraction 1 (solids) had a mass of 30.01 mg and gave 8753 counts (at 320 keV), the residual fraction 2 (mother liquor) had a mass of 34.68 mg and gave 10 949 counts (at 320 keV).

Analysis of purified material - thin layer chromatography

Thin layer chromatography was performed with the three fractions collected by the column chromatography and also with a sample before column chromatography to qualitatively analyze the separation by column chromatography. For this purpose, the (dry) samples were weighed, dissolved in a few mL of EtOAc and equivalent amounts of the solution were spotted on a thin layer plate of silica gel using a microliter pipette so that about 20 μg of substance was applied. The same solvent as used for column chromatography was used as the eluent (95% hexane and 5% EtOAc). In Figure 3.4 the thin film plates are seen under UV light: The purified complex $\text{Cr}(\text{tmhd})_3$ is in fraction 2 and there are almost no impurities visible, only a small spot that travels faster than the $\text{Cr}(\text{tmhd})_3$. Some impurities that travel more slowly are visible in the third fraction and on the right plate, on which also impurities that do not travel at all with the mobile phase are visible.

Radioanalysis - autoradiography

For the analysis of TLC plates with radioactive samples auto radiography was performed to show the distribution of ^{51}Cr along the plates. A phosphor imaging plate (NDT HCR from DÜRR NDT) was exposed to the plates packed in polyethylene bags for 4 to 7 days. A computed radiography scanner HD-CR 35 NDT from DÜRR NDT was used to read out the imaging plate. In Figure 3.5 the image of the radiography of the same two TLC plates as in Figure 3.4 can be seen. Clearly visible here are the same areas as in Figure 3.4, now representing the activities.

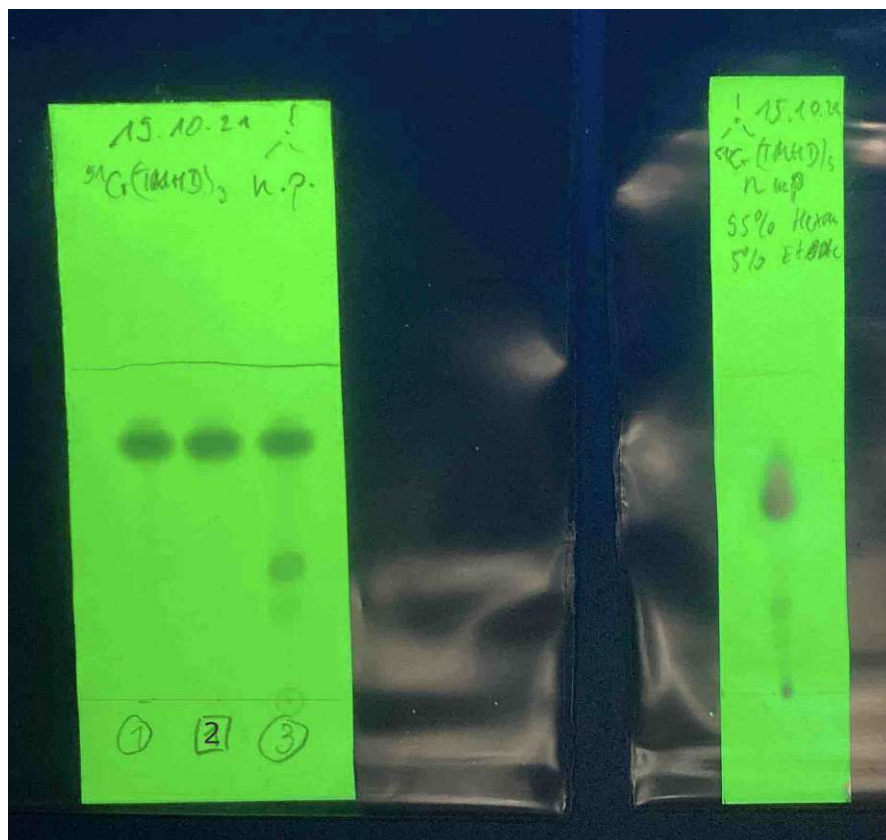


Figure 3.4: Here TLC plates are seen under UV light: on the left are the three fractions of the column chromatography (from left to right), on the right is the sample before purification by column chromatography. The purified complex $\text{Cr}(\text{tmhd})_3$ is in fraction 2 (middle) and there are almost no impurities visible, only a small spot that travels faster than the $\text{Cr}(\text{tmhd})_3$. Some impurities that travel more slowly are visible in the third fraction and on the right plate, on which also impurities that do not travel at all with the mobile phase are visible.

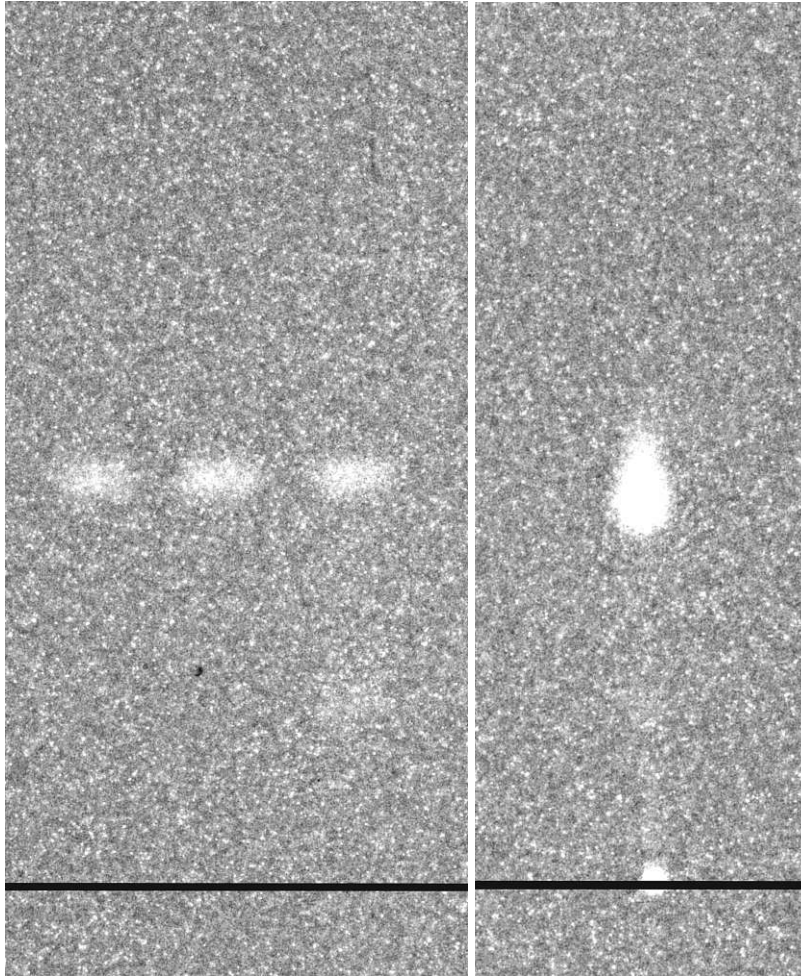


Figure 3.5: Here the radiography of the same two TLC plates which can be seen in Figure 3.4 are shown. On the left are the three fractions of the column chromatography (from left to right), on the right is the sample before purification by column chromatography. Clearly visible here are the same areas as in Figure 3.4, now representing the activities.

3.2.3 Cr(tmhd)₃ from Cr(NO₃)₃ spiked with neutron-irradiated ammonium chromate

The synthesis of unlabeled Cr(tmhd)₃ described above (see section 3.2.1) was scaled down to 500 mg (1/10 scale) and additional ⁵¹Cr in the form of irradiated ammonium chromate was added at the beginning of the synthesis.

18.4 mg (0.121 mmol) ammonium chromate were irradiated for approximately 14 h⁻¹ at a neutron flux density of about $1.7 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. After decaying (140 h), the irradiated sample was unpacked and dissolved in 3.0 mL water. To speed up the dissolution process an ultrasonic bath was used. Portions of urea (2.0282 g, 33.770 mmol), Cr(NO₃)₃·9H₂O (0.4503 g, 1.125 mmol) and 6.5 mL of ethanol were added to a 100 mL round bottomed flask. 2.4876 g of the irradiated sample dissolved in water were also added to the round-bottomed flask. The remainder (diluted to 15 mL) was set aside for gamma spectroscopic measurement (see subsection 2.2.5, using water as solvent instead of the standard procedure). The resulting mixture was heated to reflux on a 120 °C oil bath and TMHD (0.6632 g, 3.599 mmol) was added drop wise over half a minute.

The remaining procedure was the same as described in subsection 3.2.2. The mass of the dry powder directly after the synthesis (4 days after the chloroform extraction) was 737.1 mg. After dissolving in 15 mL EtOAc for gamma spectroscopic measurement and drying afterwards for 3 days, the mass was only 703.8 mg. This difference in masses was only due to the fact that the product was dissolved in chloroform and left to dry for several days, and after dissolution in another solvent (EtOAc) it was evaporated again for several days.

Chromatography on silica gel

The material collected was subjected to a column chromatographic separation as described above (section 3.2.1). The Cr(tmhd)₃ in powder form (703.8 mg) was dissolved to a concentration of about 100 mg/mL in the mobile phase. The resulting solution had a deep purple color.

After column chromatography, there was a large amount of green material apparent during the chromatographic separation. A small fraction flowed with the mobile phase and another fraction remained on top of the silica gel, some green crystals also stuck on top of the sand and on the wall of the column. The purified product weighed 602.0 mg whereas the other fractions together weighed 47.4 mg, therefore 54.4 mg remained on the column.

Recrystallization by diffusion

As described in section 3.2.2, a recrystallization with 69.4 mg was carried out. Both fractions were weighed after evaporation and then counted on the gamma spectrometer (see subsection 2.2.5). The recrystallized fraction 1 (solids) had a mass of 34.67 mg and gave 15 972 counts (at 320 keV) and the residual fraction 2 (mother liquor) had a mass of 33.47 mg and gave 15 329 counts (at 320 keV).

(Radio)analysis with TLC and autoradiography

As described in section 3.2.2 and section 3.2.2, analysis with TLC (Figure 3.6) and an autoradiography (Figure 3.7) was performed. The purified complex $\text{Cr}(\text{tmhd})_3$ is in fraction 2 and there are no impurities visible. In Figure 3.7, clearly visible are the same areas as in Figure 3.6, now representing the activities.

3.3 Results and Discussion

3.3.1 $\text{Cr}(\text{tmhd})_3$ from $\text{Cr}(\text{NO}_3)_3$

Synthesis as described in subsection 3.2.1 yielded 7.07 g, which is 106% of the theoretical yield (11.12 mmol or 6.692 g, TMHD as limiting reagent). The yield in excess of 100% is likely due to impurities in the material. The yield after the first purification step, filtration, was 6.1242 g, which is 91.5% of the theoretical calculated yield. The yield of the column chromatography step was 92.0% (641.6 mg), implying a total process yield of 84.2%. The yield is slightly larger as described in the literature [28] [29], but only comparable to a certain point, as other methods for purification are used.

3.3.2 $\text{Cr}(\text{tmhd})_3$ from $\text{Cr}(\text{NO}_3)_3$ spiked with neutron-irradiated $\text{Cr}(\text{tmhd})_3$

The amount of the dried $\text{Cr}(\text{tmhd})_3$ synthesis product recovered after extraction with chloroform (490.9 mg) is about 80% of the theoretical yield (1.0182 mmol or 612.76 mg, TMHD as limiting reagent).

302 051 counts were counted on the gamma spectrometer at 320 keV (see subsection 2.2.5), which gives a radiometric yield of 80%. The aliquot (1.0430 g) of ethanol containing irradiated $\text{Cr}(\text{tmhd})_3$ (diluted to 15 mL) gave 90 152 counts on the gamma spectrometer at 320 keV. The remainder of the solution (5.1426 g) was added to the synthesis. The total number of counts to be expected in the synthesis flask should therefore be about 444 502. However, because the TMHD

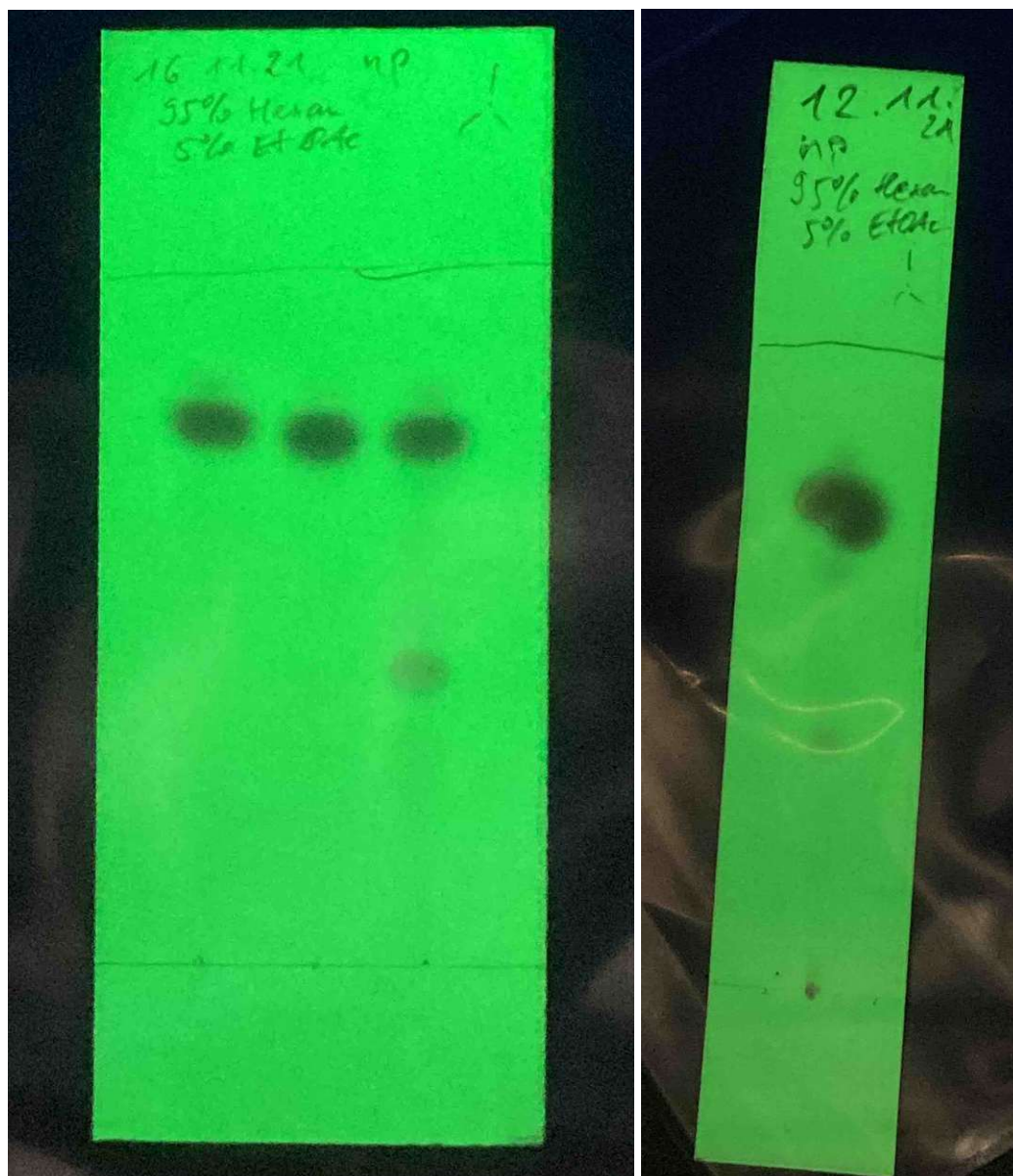


Figure 3.6: Here TLC plates are seen under UV light: on the left are the three fractions of the column chromatography (from left to right), on the right is the sample before purification by column chromatography. The purified complex $\text{Cr}(\text{tmhd})_3$ is in fraction 2 (middle) and there are no impurities visible. Some impurities that travel more slowly are visible in the third fraction and on the right plate, on which also impurities that do not travel at all with the mobile phase are visible.

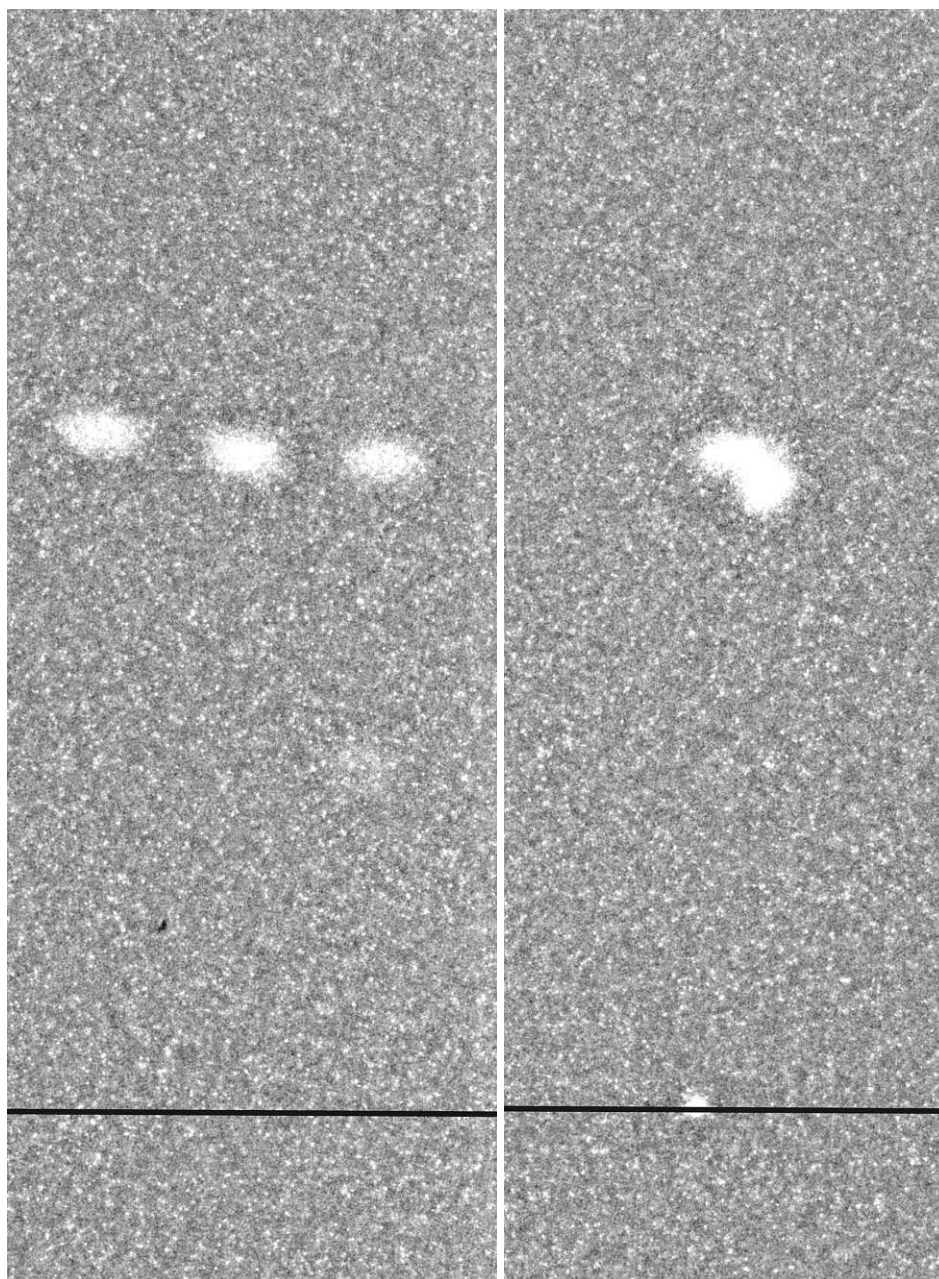


Figure 3.7: Here the radiography of the same two TLC plates which can be seen in Figure 3.6 are shown. On the left are the three fractions of the column chromatography (from left to right), on the right is the sample before purification by column chromatography. Clearly visible here are the same areas as in Figure 3.6, now representing the activities.

was a limiting reagent, only 86% (i.e. 382 272 counts) of the Cr can be in the form of $\text{Cr}(\text{tmhd})_3$, the rest of the ^{51}Cr must be in some other chemical form. This gives a radiometric yield of 80% for the dried $\text{Cr}(\text{tmhd})_3$ synthesis product.

Since the amount of product is 490.9 mg, where the theoretically calculated yield was 612.76 mg, the radiometric yield (80%) agrees very well with the mass yield (80%). As a further check, the waste from the synthesis was counted on the gamma spectrometer at 320 keV. Because the solvents of these (ethanol-water mixture respectively acetone) are not the same as those of the dissolved product (EtOAc), so the solvent density differs, and the measurement geometries of the "Rotkäppchen" are also not identical (different amount of content), the measurement is therefore only comparable to a limited extent, but it is sufficient as a rough estimate. The number of counts in the flask should be approx. 444 502 according to extrapolation using the aliquot. The measured counts of the product (302 051 counts), the ethanol water mixture (134 587 counts) and the acetone (26 762 counts) add up to 463 400 counts.

The post-column gamma spectrometry of the purified $\text{Cr}(\text{tmhd})_3$ was 142 224 counts, which is 61.9% of the ^{51}Cr applied to the column. No direct comparison to the post-synthesis measurement of $\text{Cr}(\text{tmhd})_3$ (302 051 counts) is possible, a decay correction (11 days) for ^{51}Cr is necessary. 302 051 counts (post-synthesis measurement of $\text{Cr}(\text{tmhd})_3$) give decay corrected about 229 371 and 382 272 counts (theoretical radiochemical synthetic yield) give 290 289 counts. Therefore, 61.9% of the ^{51}Cr applied is eluted from the column and 50% of the theoretical radiochemical synthetic yield of ^{51}Cr is obtained. To compare this with the mass yields, the amount of purified product collected in beaker 2 was 337.0 mg, which corresponds to 68.6% of the amount of material before the column chromatography and 55% of the theoretical synthetic yield.

In the active experiments, the recrystallization step was not used as a purification method, but to show that the ^{51}Cr distributes as the mass does. For the synthesis with additional activated $\text{Cr}(\text{tmhd})_3$, the recrystallized fraction 1 (solids) had a mass of 30.01 mg and a number of 8753 counts, the residual fraction 2 (mother liquor) had a mass of 34.68 mg and number of 10 949 counts. This gives values in counts per mg of 292 (solids) and 316 (mother liquor). The yield of the recrystallization is not of interest in this experiment, rather the specific activities (counts per mass) of the two fractions. Since the specific activities of both fractions are nearly the same, ^{51}Cr is most likely in the chemical form $\text{Cr}(\text{tmhd})_3$.

The analysis of the samples directly after the synthesis and of the three fractions of the column chromatography shows that the ^{51}Cr distributes as the mass does. The spots on the TLC plates visible under UV light match very well to the spots visible after the autoradiography. Almost no impurities are seen in

fraction 2, which contains the purified $\text{Cr}(\text{tmhd})_3$.

3.3.3 $\text{Cr}(\text{tmhd})_3$ from $\text{Cr}(\text{NO}_3)_3$ spiked with neutron-irradiated ammonium chromate

In this synthesis with additional active ammonium chromate as irradiation target, TMHD was the limiting reagent, and the overall yield (703.8 mg) was 97% of theoretical calculated. The mass of the dry powder directly after the synthesis (4 days after the chloroform extraction) was 737.1 mg. After dissolving in 15 mL EtOAc for gamma spectroscopic measurement and drying afterwards for 3 days, the mass was only the named 703.8 mg. This difference in masses was only due to the fact that the product was dissolved in chloroform and left to dry for several days, and after dissolution in another solvent (EtOAc) it was evaporated again for several days. A possible explanation is that the powder was not yet fully dry. However, since the volatility of chloroform is larger than that of EtOAc and even more time had passed during the first drying of chloroform, another possibility is that there were chloroform inclusions in the product that did not evaporate, but were displaced after dissolution in EtOAc so that the mass was lower afterwards.

The synthesis product produced 626 878 counts at 320 keV, which gives a radiochemical yield of 86%. Of the total solution of irradiated $(\text{NH}_4)_2\text{CrO}_4$ in water, 2.4876 g was added to the synthesis and the remainder (0.5444 g) was used as an aliquot to determine how much ^{51}Cr had been in the sample and how much was added to the synthesis accordingly. The measured number of counts of the aliquot were 165 286 at 320 keV. The total number of counts to be expected in the synthesis flask should therefore be about 755 264 counts. However, because TMHD is the limiting reagent, only 96% (i.e. 725 053 counts) of this can be in the form of $\text{Cr}(\text{tmhd})_3$, the rest of the ^{51}Cr must be in some other chemical form.

602.0 mg of the amount applied to the column was recovered, which is a yield of 85.5% for the column chromatography step and a total synthetic yield of 83.4%. The post-column counts were 454 461, which gives a radiochemical yield of 86.4% for the column chromatography step and a total theoretical radiochemical yield of 74.7%. The time between the post-synthesis measurement and the post-column measurement was about 7 days, the measurements have to be decay-corrected. The decay-corrected number of counts of the product before the column is about 526 151 counts, and the theoretically possible value is 608 551 counts, respectively.

The recrystallized fraction 1 had a mass of 34.67 mg with a number of 15 972 counts and the residual fraction 2 had a mass of 33.47 mg with a number of 15 329 counts. This gives values in counts per mg of 461 (solids) and 458 (mother

	$^{51}\text{Cr}(\text{tmhd})_3$	$(\text{NH}_4)_2^{51}\text{CrO}_4$
Synthesis [mass yield]	80%	97%
Synthesis [radiometric yield]	80%	86%
Column [mass yield]	69%	86%
Column [radiometric yield]	62%	86%
Recrystallization (solid) [counts/mg]	292	461
Recrystallization (mother liquor) [counts/mg]	316	458

Table 3.1: Mass yields and radiometric yields after each experimental step and recrystallization ratios between counts and masses of the irradiation targets $\text{Cr}(\text{tmhd})_3$ and ammonium chromate

liquor). Since the specific activities (counts per mass) of both fractions are nearly the same, ^{51}Cr is most likely in the chemical form $\text{Cr}(\text{tmhd})_3$. The analysis with TLC and the autoradiography confirms that.

3.3.4 Comparison between the two irradiation targets $\text{Cr}(\text{tmhd})_3$ and ammonium chromate

Both irradiation targets show good agreement between the behavior of the mass and ^{51}Cr in the respective steps. In Table 3.1 the mass and radiometric yields of both irradiation targets are compared to each other. The percentages always refer only to the latest step. Here it is not of major relevance how the yields of one irradiation target are compared to the other, but that the masses and radiometric yields are as similar as possible. This indicates the same behavior of mass (all Cr isotopes) and ^{51}Cr . This is best for the synthesis with added ammonium chromate.

TLC and radiography are also strong indicators that mass behaves the same as ^{51}Cr . In TLC, the different chemical components can be separated and visualised under UV light. A TLC immediately after synthesis and another with the three fractions of the column chromatography show the existence of impurities and indicate that column chromatography as a purification step can separate most impurities. Radiography then allows a qualitative evaluation of the local activity distribution on the thin film plates. It is therefore possible to check which of the chemical substances contains the activity.

3.4 Conclusion

Two experiments were compared with each other. One synthesis of $\text{Cr}(\text{tmhd})_3$ was performed with neutron-irradiated product $\text{Cr}(\text{tmhd})_3$ and another with neutron-irradiated ammonium chromate.

The aim was to establish the incorporation of ^{51}Cr regardless of the chemical state of the active ^{51}Cr introduced. Incorporation of the radioisotope in the synthesized material implies that the activity introduced is present in product form at the end of the synthesis. Since the mass yield and the radiometric yield for each purification and analysis step were very similar in both experiments, it can reasonably be assumed that both synthesis approaches fulfil the aim. The synthesis with irradiated ammonium chromate shows the best correspondence. The synthetic mass yields are also comparable to the inactive models (see subsection 3.2.1, so the addition of the other substances does not seem to interfere with the synthesis.

4 Chemical separation (enrichment) of neutron-induced ^{51}Cr from bulk Cr-containing target materials

4.1 Introduction

In this chapter methods of increasing the specific activity of chromium are described. The Szilard-Chalmers effect is used to achieve isotope separation by chemical methods from bulk Cr-containing target materials. Chromium compounds irradiated in a reactor were taken as starting material. As one possible target material is organic ($\text{Cr}(\text{tmhd})_3$) and the other is inorganic (ammonium chromate), these require contrary procedures in enrichment because of different chemical properties. The aim is to achieve as much enrichment of ^{51}Cr as possible.

Firstly, one method of enrichment is using the $\text{Cr}(\text{tmhd})_3$ complex itself as a starting point for isotope separation. Advantage is taken of the fact that after irradiation of $\text{Cr}(\text{tmhd})_3$, more than 90% of the ^{51}Cr is in other chemical form than $\text{Cr}(\text{tmhd})_3$ [18].

Another method is presented that uses ammonium chromate as an irradiation target substance. As described in the literature, ammonium chromate or potassium chromate are suitable irradiation target materials that can be used in chemical separation processes (enrichment) [30][31]. Separation is achieved performing a liquid-liquid extraction with methyl isobutyl ketone. As a preliminary experiment, the performance of a liquid-liquid extraction with inactive ammonium chromate is explained and the attempt of an upscaling of the procedure with larger amount of substance. This scaling is necessary because a larger amount of ammonium chromate is needed to maximize the activity produced. Equation 2.5 transformed gives the following equation for the required mass m of chromium at the chosen activity A , given irradiation time t_i , decay time t_d , molar mass M , isotopic abundance H , cross section σ , Avogadro number N_A and neutron flux density Φ .

$$m = \frac{AMe^{\lambda t_d}}{\Phi\sigma HN_A(1 - e^{-\lambda t_i})} \quad (4.1)$$

For example, if 40 MBq are desired, using $\sigma = 15$ barn, $M = 51.996$ g/mol, $H_{Cr-50} = 0.04345$ and $\lambda = 2.8958 \times 10^{-7} \text{ s}^{-1}$, 243.8 mg Cr are required ¹. It must also be taken into account that 713 mg ammonium chromate and 2.82 g Cr(tmhd)₃ have to be used for this amount of Cr.

4.2 Experimental methods

4.2.1 Chemical separation (enrichment) of neutron-induced ⁵¹Cr from irradiated Cr(tmhd)₃ using chromatography on silica gel

About 70 mg (73.5 mg) of chromium complex Cr(tmhd)₃, manufactured by Aldrich Company, was irradiated for about 14 h ² at a neutron flux density of about $1.7 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. After about 90 h of decay, the sample was unpacked and dissolved in 2 mL of a mixture of hexane (95%) and ethyl acetate (5%). The irradiated Cr(tmhd)₃ sample was measured at the gamma spectrometer (see subsection 2.2.5) in the usual 40 mL container ("Rotkäppchen"), but it had only 2 mL solvent as content. Afterwards, column chromatography was performed as described in section 3.2.1. In the column chromatography, as much of the lilac fraction as possible was collected in a beaker and then the eluent was changed and ethanol was poured into the top of the column instead of the hexane ethyl acetate mixture. The ethanol had a much lower flow rate. The green impurities that had stuck at the top of the column when using the hexane ethyl acetate mixture were washed off the column with the ethanol. The entire ethanol fraction was collected in a beaker and the packed column was drained into a "Gelbkäppchen".

After evaporation of the solvents, the fractions were weighed. 69.5 mg of the original sample was in the Cr(tmhd)₃ fraction after the column, 5.3 mg was in the ethanol fraction. Afterwards the samples were dissolved in 2 mL solvent (hexane ethyl acetate mixture for Cr(tmhd)₃ and ethanol for the ethanol fraction) and transferred to a "Rotkäppchen" to measure it on the gamma spectrometer. For comparison to the initial measurement (above), again only 2 mL solvent was used.

¹14 h irradiation time at a neutron flux density of about $1.7 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ and 120 h decay time

²2 x 7 h with a 17 h break in between two consecutive reactor operation days.

4.2.2 Liquid-liquid extraction of inactive ammonium chromate with MIBK

Experimental description

About 35 mg of ammonium chromate was dissolved in 15 mL 1 M Hydrochloric acid (HCl) and poured into a separating funnel. The solution had a yellow color. As extraction solvent, methyl isobutyl ketone (MIBK in the following, $(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{O})\text{CH}_3$) is used, which is immiscible with water. The hexavalent chromate is extracted from the aqueous solution into the organic phase. 5 mL of MIBK were added to the funnel. Then the funnel was shaken to maximize the shared surface area of the liquids and then it was left at rest to allow the two phases to separate again. The aqueous phase settled to the bottom because the MIBK has a lower density. The upper organic phase was noticeably yellowish and the lower aqueous paler than before. The two phases were collected in separate beakers and the aqueous phase was returned to the funnel. The procedure was repeated with another 5 mL of MIBK until the aqueous solution was completely colorless. This required a total of four cycles.

Liquid-liquid extraction of larger amounts of ammonium chromate with MIBK

The extraction was scaled up to test the extraction efficiency (number of extraction cycles) with larger amounts (1 g) of ammonium chromate. A stock solution of ammonium chromate in 1 M HCl was produced to avoid multiple weighing. About 1 g of ammonium chromate (1.001 g) were weighed into a small glass flask and 20 mL 1 M HCl were added. The arising solution had a deep yellowish orange color (see Figure 4.1).

The first step was the scaling up to 100 mg chromate, for which 2 mL of the stock solution were used, diluted to 15 mL of HCl. In total, five extractions with MIBK (5 mL each) were necessary to achieve a colorless aqueous solution. The second round was done with 250 mg chromate (5 mL stock solution) and six extractions were necessary. For the third round (600 mg chromate, which was 12 mL stock solution) 10 mL MIBK instead of 5 mL were used at each extraction step to speed up the process. The fourth extraction created a slight emulsion between the two phases and the fifth extraction a strong emulsion (see Figure 4.2). After the sixth extraction almost no color difference between the two phases were apparent.

For the next scaling step, extraction with 2 M HCl was attempted to avoid emulsion formation. About 1.2 g (1.1948 g) of ammonium chromate was dissolved in 15 mL of 2 M HCl, and each step of the extraction was performed with

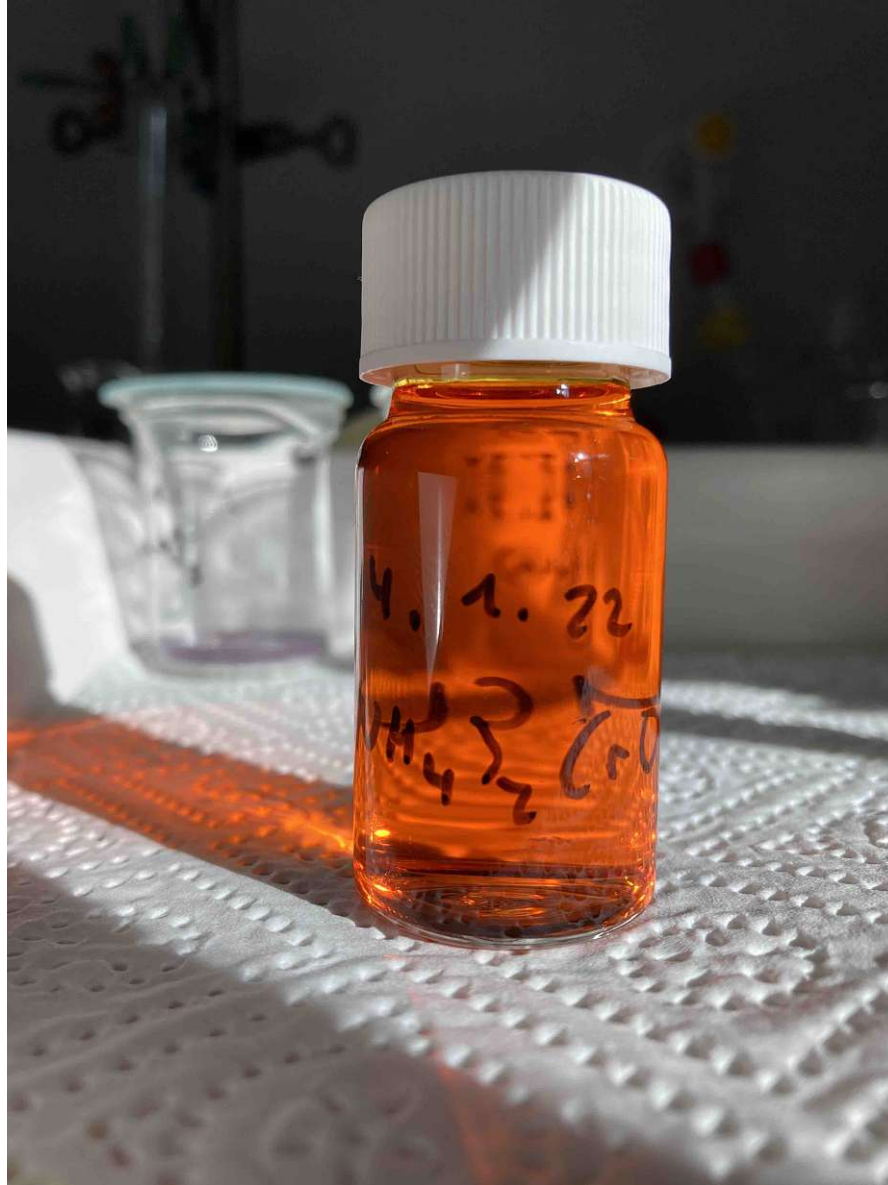


Figure 4.1: Here the deep orange solution of 1 g ammonium chromate in 20 mL 1 M HCl can be seen.



Figure 4.2: Liquid-liquid extraction of ammonium chromate in HCL in methyl isobutyl ketone: the lower aqueous phase is already almost colorless, the upper organic phase is yellowish. In between, a whitish emulsion can be seen in which the two phases are not separated from each other.

10 mL of MIBK. Only at the sixth extraction step a slight emulsion formation was visible, afterwards the aqueous solution was only slightly yellowish, almost colorless.

4.2.3 Chemical separation (enrichment) of neutron-induced ^{51}Cr from irradiated ammonium chromate using liquid-liquid extraction with MIBK

Three experiments were carried out, each with different amounts of ammonium chromate and different irradiation times, i.e. different activities. The first experiment was performed with small amounts of ammonium chromate and low activity. The second and third experiment had initially the same amount of substance, however some ammonium chromate was lost in the third experiment. In the third experiment the irradiation time was longer than in the second, i.e. the third experiment had larger activity. The following activities are rough estimates calculated with Equation 4.1 and the given amounts of material and irradiation times.

36 mg ammonium chromate with 2 MBq ^{51}Cr

35.9 mg of ammonium chromate were irradiated for approximately 14 h² at a neutron flux density of about $1.7 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. The sample was dissolved in 16 mL 1 M HCl, of which 1 mL (1.144 g) (diluted to 15 mL) served as an aliquot for gamma spectroscopic measurement (see subsection 2.2.5) and 15 mL (15.384 g) were transferred to the separatory funnel for liquid-liquid extraction. The extraction was performed as in the down-scaled experiment (5 mL MIBK for each step). Four runs to a completely colorless aqueous solution were required. After the last extraction, the MIBK fraction was used in another liquid-liquid extraction, now using H₂O (3x5 mL) as extractant, for better comparison (similar densities of the solvent) of the gamma spectroscopic measurements. In the following experiments, this last step (back extraction) was omitted. All fractions (HCl, H₂O and MIBK) were counted at the gamma spectrometer at 320 keV. Afterwards, the HCl fraction was poured into a 100 mL round bottom flask to perform a radiosynthesis of Cr(tmhd)₃ with enriched ^{51}Cr (see subsection 5.2.2).

600 mg ammonium chromate with 5 MBq ^{51}Cr

601.4 mg of ammonium chromate were irradiated for approximately 4 h at a neutron flux density of about $1.7 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. The sample was dissolved in 16 mL 2 M HCl, of which 1 mL (1.360 g) (diluted to 15 mL) served as an aliquot for

gamma spectroscopic measurement and 15 mL (15.72 g) were transferred to the separatory funnel for liquid-liquid extraction. The extraction was performed as in the upscaled experiment (10 mL MIBK for each step). Five runs to a completely colorless aqueous solution were required. No back extraction with H₂O was carried out. After the last extraction, the fractions (HCl (aqueous) and a 15 mL aliquot of MIBK) were counted at the gamma spectrometer at 320 keV. Afterwards, the aqueous fraction was poured into a 50 mL round bottom flask to perform a radiosynthesis of Cr(tmhd)₃ with enriched ⁵¹Cr (see subsection 5.2.2).

600 mg ammonium chromate with 25 MBq ⁵¹Cr

About 600 mg (607.1 mg) ammonium chromate were irradiated for approximately 14 h² at a neutron flux density of about $1.7 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. After noticing during sample unpacking (decay time about 66 h) that the sample capsule had opened during irradiation, a portion of the sample (about 462 mg) was recovered from inside the dry irradiation capsule by dissolving in 2 M HCl and the remainder was lost. The usable portion was dissolved in 31 mL 2 M HCl, of which 1 mL (1.133 g) (diluted to 15 mL) served as an aliquot for gamma spectroscopic measurement and 15 mL (15.567 g) were transferred to the separatory funnel for liquid-liquid extraction. These corresponded to approximately 224 mg of ammonium chromate. The extraction was performed as in the upscaled experiment (10 mL MIBK for each step). Four runs to a completely colorless aqueous solution were required. After the last extraction, the fractions (aqueous and a 15 mL aliquot of MIBK) were counted at the gamma spectrometer at 320 keV. Afterwards, the aqueous fraction was poured into a 50 mL round bottom flask to perform an active synthesis of Cr(tmhd)₃ with enriched ⁵¹Cr (see subsection 5.2.2).

4.3 Results and Discussion

4.3.1 Chemical separation (enrichment) of neutron-induced ⁵¹Cr from Cr(tmhd)₃ using chromatography on silica gel

The irradiated Cr(tmhd)₃ sample, containing only 2 mL (instead of 15 mL) solvent content in the usual 40 mL container ("Rotkäppchen") (see subsection 2.2.5), produced 1 830 496 counts at 320 keV. To ensure comparability, all future comparison measurements must also be made with the same amount of solvent, so the geometry is not changed.

After column chromatography, almost the entire mass (69.5 mg or 94.6%) of the original sample was still in the form of Cr(tmhd)₃, only 5.3 mg (or 7.2%)

was in the ethanol fraction, which contained the green impurities of the column. This is a limiting factor for enrichment of ^{51}Cr , as a macroscopic amount of inactive chromium is part of the enriched fraction. For comparability in the measurement on the gamma spectrometer only 2 mL solvent was used instead of the usual 15 mL (see subsection 2.2.5). However, the fact that different solvents (ethanol and EtOAc) were used, i.e. that the solvent densities differ, limits the comparability.

197 771 counts ($\text{Cr}(\text{tmhd})_3$ fraction), 968 485 counts (ethanol fraction) and 541 601 counts ("Gelbkäppchen" containing the dried column material, i.e. sand and silica gel) were counted on the gamma spectrometer at 320 keV. The sum of these three measurements (1 707 857 counts) slightly differs from the decay-corrected value of the measurement of the irradiated sample (1 830 496 gives decay-corrected 1 777 829 counts), because the "Gelbkäppchen" geometry is not the same geometry as the "Rotkäppchen" and different solvents in the "Rotkäppchen" were used. The measurements showed that only 11% of the total ^{51}Cr was in the $\text{Cr}(\text{tmhd})_3$ fraction, the remainder was in some other chemical form after irradiation and therefore remained on the column during chromatography. With ethanol, about 55% of the total ^{51}Cr induced via neutron activation could be washed off the column.

4.3.2 Liquid-liquid extraction of inactive ammonium chromate with MIBK

In general, the procedure had to be modified only slightly to be usable after scaling. With larger amounts of ammonium chromate, more MIBK was used per extraction step (10 mL instead of 5 mL) and more MIBK was needed to complete the extraction (4 to 6 runs instead of 3), which shows a reduced extraction efficiency. Over the course of multiple extractions, the boundary between the liquid phases becomes poorly defined (emulsion, see Figure 4.2). This seems to be due to acid depletion, which was avoided by using 2 M HCl.

4.3.3 Chemical separation (enrichment) of neutron-induced ^{51}Cr from ammonium chromate using liquid-liquid extraction with MIBK

The liquid-liquid extraction did not cause major problems, only sometimes there were slight indications of an emulsion. The amount of ^{51}Cr in the enriched aqueous phase measured at the gamma spectrometer (see subsection 2.2.5) was about 70-80% of the total amount of ^{51}Cr added in the beginning.

Amount of irradiated ammonium chromate used in the liquid-liquid extraction	36 mg	601 mg	224 mg
Activity in aqueous fraction [% of the total activity]	78%	70%	72%
Activity in MIBK fraction [% of the total activity]	17%	17%	21%

Table 4.1: Isotopic separation yields using liquid-liquid extraction of ammonium chromate with MIBK for three different experiments

For the first experiment (section 4.2.3), 162 006 counts were counted at 320 keV for the aliquot of the irradiated sample (1.144 g). After the liquid-liquid extraction, the different fractions were counted on the gamma spectrometer: the H₂O fraction had 330 499 counts, which is about 17% of the calculated value added at the beginning of the experiment. The measured counts of the HCl fraction are 1 554 600 counts, which gives a yield of about 78% and the MIBK fraction had 450 counts. In this experiment a back extraction using H₂O was used to ensure comparability between the ⁵¹Cr enriched HCl fraction and the H₂O fraction containing the residual ⁵¹Cr. In the following experiments this step was omitted, as the result of interest is the number of counts in the ⁵¹Cr enriched HCl fraction, which will be used in subsection 5.2.2 for the next experiment. The MIBK fraction can be used as an approximate confirmation that the liquid-liquid extraction yield does not deviate significantly from the previous experiments.

For the second experiment (section 4.2.3), 751 182 counts were counted at 320 keV for the aliquot of the irradiated sample (1.360 g). After the liquid-liquid extraction with 15.72 g amounts of substance, the different fractions were counted on the gamma spectrometer: the MIBK fraction (measurement of an 15 mL aliquot of total 50 mL) had 452 354 counts. The activity in the entire MIBK is therefore about 17% of the calculated value added at the beginning of the experiment. The measured counts of the aqueous fraction are 6 083 209 counts, which gives a yield of about 70%.

For the third experiment (section 4.2.3), 858 808 counts were counted at 320 keV for the aliquot of the irradiated sample (1.133 g). After the liquid-liquid extraction with 15.567 g amounts of substance, the different fractions were counted on the gamma spectrometer: the MIBK fraction (measurement of an 15 mL aliquot of total 40 mL) had 929 116 counts. The activity in the entire MIBK is therefore about 21% of the calculated value added at the beginning of the experiment. The measured counts of the aqueous fraction are 8 492 027 counts, which gives a yield of about 72%. Table 4.1 shows a brief overview of the important yields for the three different experiments.

One challenge when working with larger activities is increased protective measures. The first and most important precaution is increased distance. However, hand contact with the separating funnel cannot be avoided when performing liquid-liquid extraction. For this reason, after irradiating a large amount of ammonium chromate, the amount of activity was reduced by dividing the amount of ammonium chromate rather than using the total amount at once (see section 4.2.3).

4.3.4 Comparison of the methods of neutron-induced ^{51}Cr enrichment from bulk Cr-containing target materials

Two principal methods for the enrichment of ^{51}Cr were tested. Firstly, these experiments were done on a small scale to decide whether they worked at all. After both ways led to the goal in principle, the results were used to consider which way was more suitable for scaling up to larger amounts of material and activity. In both experiments there were indications, that inactive material was still present in the chemically separated fraction enriched with ^{51}Cr . There were a few reasons why liquid-liquid extraction was preferred, especially when it was taken into account that the aim was to carry out the experiment with more activity and materials. On the one hand, the radiometric yields with ammonium chromate (about 70-80%) was significantly greater than that with $\text{Cr}(\text{tmhd})_3$ (about 50%). This was because a large amount of the ^{51}Cr produced in the irradiated $\text{Cr}(\text{tmhd})_3$ got stuck on the column and could not all be washed down with ethanol. Another reason is that even on a small scale with only 70 mg $\text{Cr}(\text{tmhd})_3$, not a small amount of ethanol had to be used for the column to be completely washed and for the ^{51}Cr to be collected. With larger activities and thus more irradiated $\text{Cr}(\text{tmhd})_3$, a larger column and thus significantly more pure ethanol would have to be used. In order to avoid unnecessary and expensive material costs, the other option with ammonium chromate was the better choice. In addition, larger quantities of ammonium chromate were also more readily available in the laboratory and cheaper than $\text{Cr}(\text{tmhd})_3$. An open question for both enrichment methods is to determine the ratio of active ^{51}Cr to other chromium isotopes after a successful enrichment. This would be a measurement of how efficiently the enrichment works and could possibly be done with a further neutron activation analysis.

5 Application of chemically separated ^{51}Cr enriched material in a radiosynthesis of $\text{Cr}(\text{tmhd})_3$

5.1 Introduction

In this chapter, the application of separated ^{51}Cr from bulk Cr-containing target materials is described. The ^{51}Cr enriched products from the experiments in chapter 4 were added to a synthesis of $\text{Cr}(\text{tmhd})_3$. The procedure for the radiosynthesis of $\text{Cr}(\text{tmhd})_3$ is the same as in subsection 3.2.2 respectively subsection 3.2.3. Firstly, a $\text{Cr}(\text{tmhd})_3$ radiosynthesis with ^{51}Cr enriched material performing a column-chromatographic step on irradiated $\text{Cr}(\text{tmhd})_3$ is presented. Subsequently, the procedure with ^{51}Cr enriched material using liquid-liquid extraction of irradiated ammonium chromate with MIBK is described, whereby it is explained how the ^{51}Cr enriched sample must be prepared so that it can be used for $\text{Cr}(\text{tmhd})_3$ synthesis. The problems that occurred when increased activities (i.e. increased amounts of substances in the enrichment process) were added to a down-scaled synthesis will be discussed.

5.2 Experimental methods

5.2.1 $\text{Cr}(\text{tmhd})_3$ synthesis with ^{51}Cr enriched material from $\text{Cr}(\text{tmhd})_3$

After chromatography on silica gel with irradiated $\text{Cr}(\text{tmhd})_3$ (see subsection 4.2.1), the ^{51}Cr enriched material (ethanol fraction) is applied in a radiosynthesis of $\text{Cr}(\text{tmhd})_3$ (see subsection 3.2.2). The synthesis was performed in a scaling to 250 mg of product, adding the ^{51}Cr enriched ethanol fraction with 2 mL ethanol as ^{51}Cr source. The amounts weighed were 224.9 mg (0.5620 mmol) $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 1.0270 g (17.100 mmol) urea, 2.5 mL H_2O , 4.5 mL EtOH and 0.3189 g (1.731 mmol) TMHD. After the chloroform extraction, the mass of the

extracted and dried fraction was 345.6 mg. A column chromatography was then carried out and the different fractions were analyzed by thin layer chromatography and radiography, and the purified $\text{Cr}(\text{tmhd})_3$ fraction was dried and weighed. The mass of the purified $\text{Cr}(\text{tmhd})_3$ after the column was 266.0 mg. Then the sample was diluted with 15 mL ethanol and counted on the gamma spectrometer. Here, the gamma spectroscopic measurement was carried out in the reproducible C15 geometry with 15 mL solvent (ethanol) due to the standard procedures (see subsection 2.2.5). However, because in subsection 4.3.1, all gamma spectroscopic measurements were carried out in the same 40 mL container ("Rotkäppchen") but only with 2 mL ethanol as content, an aliquot of 2 mL (1.7469 g or 13.1% (weight)) of the total 15 mL (13.3372 g) $\text{Cr}(\text{tmhd})_3$ product fraction was used for comparison with the measurements of subsection 4.3.1.

5.2.2 $\text{Cr}(\text{tmhd})_3$ synthesis with ^{51}Cr enriched material from ammonium chromate

After liquid-liquid extraction of irradiated ammonium chromate with MIBK (see subsection 4.2.3), the ^{51}Cr enriched material (aqueous HCl solution) is applied in a radiosynthesis of $\text{Cr}(\text{tmhd})_3$. To drive out the hydrochloric acid so that the $\text{Cr}(\text{tmhd})_3$ synthesis could be carried out as described in chapter 3 or with further scaling to 25 mg of product, the aqueous fraction of the liquid-liquid extraction was heated to 120 °C in the round bottom flask with an oil bath. During this process, a nitrogen gas cylinder was used to set a permanent gas flow through the round bottom flask so that the HCl could evaporate as efficiently as possible. After several hours, a white powder with some green residue remained at the bottom of the flask, in which ammonium and chloride could be detected. For the detection procedure see [32]. Three experiments in subsection 4.2.3 were carried out, with different amounts of ammonium chromate and different irradiation times, i.e. different activities. The experiments following are carried out with different $\text{Cr}(\text{tmhd})_3$ synthesis scaling.

36 mg ammonium chromate with 2 MBq ^{51}Cr

In the first experiment (section 4.2.3) 36 mg ammonium chromate were used as a starting point for the liquid-liquid extraction. After drying the aqueous fraction a $\text{Cr}(\text{tmhd})_3$ synthesis (see subsection 3.2.3) with scale to 250 mg product was performed.

The amounts weighed were 225.1 mg (0.5626 mmol) $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 1.0133 g (16.871 mmol) urea, 2.5 mL H_2O , 6.5 mL EtOH and 0.2999 g (1.627 mmol) TMHD. After the chloroform extraction, the mass of the extracted and dried fraction

was 318.6 mg. A column chromatography was then carried out and the different fractions were analyzed by thin layer chromatography, and the purified $\text{Cr}(\text{tmhd})_3$ fraction was dried, weighed and then diluted with 15 mL of EtOAc to be counted on the gamma spectrometer (see subsection 2.2.5). The mass of the purified $\text{Cr}(\text{tmhd})_3$ after the column was 248.3 mg.

600 mg ammonium chromate with 5 MBq ^{51}Cr

As a next attempt, an order of magnitude larger amount of irradiated ammonium chromate (600 mg) was used in the liquid-liquid extraction (section 4.2.3) and the amount of the $\text{Cr}(\text{tmhd})_3$ synthesis was decreased by an order of magnitude (50 mg).

The amounts weighed were 33.34 mg (0.08332 mmol) $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 202.7 mg (3.375 mmol) urea, 2.5 mL H_2O , 6.5 mL EtOH and 0.052 mL (0.2492 mmol) TMHD. At the end of the synthesis, a lot of green substance was visible and hardly any lilac product. After the chloroform extraction, the mass of the extracted and dried fraction was 17.46 mg. The experiment was discontinued because the yield was too low.

224 mg ammonium chromate with 10 MBq ^{51}Cr

Afterwards, another $\text{Cr}(\text{tmhd})_3$ synthesis was carried out with a likewise large amount of irradiated ammonium chromate (about 224 mg, section 4.2.3), but with increased activity and decreased $\text{Cr}(\text{tmhd})_3$ synthesis amount (25 mg).

For the synthesis, 16.6 mg (0.0415 mmol) $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and about 70 mg (1.2 mmol) urea were weighed and added to the flask together with 4.2 mL EtOH and 2.5 mL H_2O . In addition, 2.3 mL of a TMHD solution in ethanol (10.456 g/l) (equivalent to 0.13 mmol THMD) was added after reaching reflux. At the end of the synthesis, a lot of green substance was visible and hardly any lilac product. 10 mL of H_2O was added to precipitate the small amount of product and 20 mL of chloroform was added for extraction. The chloroform with the $\text{Cr}(\text{tmhd})_3$ was extracted with a syringe into a beaker for drying and weighing, then the water and ethanol mixture was transferred to a "Rotkappchen" for gamma spectroscopic measurement (see subsection 2.2.5) and the reaction flask was washed with 15 mL of acetone, also counting on the gamma spectrometer. Ammonium and chloride were detected in the ethanol water mixture [32]. The mass of the extracted and dried $\text{Cr}(\text{tmhd})_3$ fraction was 9.68 mg and it was transferred with EtOAc into a "Rotkappchen" and diluted to 15 mL for gamma spectroscopic measurement. The experiment was discontinued because the yield was too low.

Cr(tmhd)₃ synthesis using liquid-liquid extraction of inactive ammonium chromate with MIBK

For a control experiment to test why the last two syntheses resulted in such low yields, the whole experiment, including section 4.2.3 was repeated with inactive ammonium chromate, i.e. performing a liquid-liquid extraction of ammonium chromate with MIBK and using the resulting aqueous fraction after drying in a Cr(tmhd)₃ synthesis. 227.9 mg of ammonium chromate was dissolved in 15 mL 2 mol/L HCl and transferred to the separatory funnel for liquid-liquid extraction. The extraction was performed as in the upscaled inactive experiment, i.e., with 10 mL of MIBK each (see section 4.2.2). Five runs to a completely colorless aqueous solution were required. Afterwards, the aqueous fraction was poured into a 50 mL round bottom flask, dried and a Cr(tmhd)₃ synthesis was carried out by bachelor student Johannes Reithofer.

5.3 Results and discussion

5.3.1 Cr(tmhd)₃ synthesis with ⁵¹Cr enriched material from Cr(tmhd)₃

The mass after the chloroform extraction at the end of the Cr(tmhd)₃ synthesis was 345.6 mg, whereas the calculated maximum theoretical yield was 338.2 mg. After a column chromatography, the mass of the sample was 266.0 mg, which is 79% of the theoretical yield. The post-column radiometric yield of the purified Cr(tmhd)₃ was 77.7% of the amount of added ⁵¹Cr to the synthesis at the beginning (using decay correction of the results in subsection 4.3.1 and the 2 mL aliquot of the purified Cr(tmhd)₃). The good agreement of mass yield and radiometric yield after column chromatography indicates that the ⁵¹Cr mostly was in chemical form of Cr(tmhd)₃, which is confirmed by the TLC plates and the radiography of the TLC plates. Also the yields are comparable to the yields of an inactive Cr(tmhd)₃ synthesis (see subsection 3.3.1) and to the yields of the ⁵¹Cr labeled Cr(tmhd)₃ synthesis (see subsection 3.3.2 and subsection 3.3.3).

5.3.2 Cr(tmhd)₃ synthesis with ⁵¹Cr enriched material from ammonium chromate

36 mg **ammonium chromate with 2 MBq ⁵¹Cr**

The mass after the chloroform extraction at the end of the Cr(tmhd)₃ synthesis was 318.6 mg, whereas the calculated maximum theoretical yield was 326.5 mg.

After a column chromatography, the mass of the sample was 248.3 mg, which is 76.1% of the theoretical yield. The sample containing the $\text{Cr}(\text{tmhd})_3$ synthesis product produced 827 094 counts at 320 keV. This gives a post-column radiometric yield of 78.4% (using TMHD as limiting factor and decay correction of the results in subsection 4.3.3, which gives 1 094 009 counts added to the synthesis). The good agreement of mass yield and radiometric yield after column chromatography indicates that the ^{51}Cr mostly was in chemical form of $\text{Cr}(\text{tmhd})_3$, which is confirmed by the TLC plates and the radiography of the TLC plates.

600 mg ammonium chromate with 5 MBq ^{51}Cr

The mass after the chloroform extraction at the end of the $\text{Cr}(\text{tmhd})_3$ synthesis was 17.46 mg, whereas the calculated maximum theoretical yield was 49.98 mg, which gives a yield of 34.9%. The sample containing the $\text{Cr}(\text{tmhd})_3$ synthesis product produced 1 213 689 counts at 320 keV. This gives a post-column radiometric yield of 24.4% (using decay correction of the results in subsection 4.3.3, which gives 4 995 180 counts added to the synthesis). In the waste fractions of the $\text{Cr}(\text{tmhd})_3$ synthesis (ethanol and acetone fractions after the chloroform extraction), solids were clearly visible settling at the bottom of the "Rotkäppchen". Most of the ^{51}Cr was found in the waste fractions. One assumption for this reduced efficiency both for the mass and the radiometric yield in the synthesis is the large amount of ammonium chloride that is produced as a by-product during the liquid-liquid extraction. After dissolving ammonium chromate in hydrochloric acid, the chromium is extracted in the form of chromic acid with MIBK, leaving behind ammonium and chloride ions. These could be detected after the liquid-liquid extraction and also in the ethanol-water mixture after the $\text{Cr}(\text{tmhd})_3$ synthesis.

224 mg ammonium chromate with 10 MBq ^{51}Cr

The mass after the chloroform extraction at the end of the $\text{Cr}(\text{tmhd})_3$ synthesis was 9.68 mg, whereas the calculated maximum theoretical yield was 24.97 mg, which gives a yield of 38.8%. The sample containing the $\text{Cr}(\text{tmhd})_3$ synthesis product produced 1 774 791 counts at 320 keV. This gives a post-column radiometric yield of 22.5% and a count rate of 5916 countspersecond (using decay correction of the results in subsection 4.3.3, which gives 7 886 089 counts added to the synthesis).

In both the ethanol and acetone fractions, solids were clearly visible settling at the bottom of the "Rotkäppchen". Therefore, the results of the usual 5 minutes measurement time (subsection 2.2.5) (ethanol 6 983 383 counts (count rate of 23 278 countspersecond) and acetone 2 445 237 counts (count rate of

8151 countspersecond)) were clearly overestimated. The "Rotkäppchen" were therefore shaken to stir up the solids and then a short measurement was carried out quickly so that the ^{51}Cr could be expected to be as homogeneously distributed as possible. The count rate was 16 257 countspersecond for the ethanol and 4666 countspersecond. The extrapolated values would be 60% (ethanol) and 17% (acetone), which adds up with the product to 102%, so the results are still a bit overestimated, but match quite good. Here a reduced efficiency both for the mass and the radiometric yield is found again, likely due to the large amount of ammonium chloride after liquid-liquid extraction.

Cr(tmhd)₃ synthesis using liquid-liquid extraction of inactive ammonium chromate with MIBK

The mass after the chloroform extraction at the end of the Cr(tmhd)₃ synthesis gave a yield of about 30%. Again, the very low efficiency comparing to a down-scaled Cr(tmhd)₃ synthesis is most likely due to the large amounts of ammonium chloride after liquid-liquid extraction. Both ammonium and chloride ions could be detected in the aqueous solution after the liquid-liquid extraction and also in the ethanol-water mixture after the Cr(tmhd)₃ synthesis.

5.3.3 Comparison of the different Cr(tmhd)₃ synthesis with ^{51}Cr enriched material using liquid-liquid extraction of irradiated ammonium chromate with MIBK

Initially, the Cr(tmhd)₃ synthesis with ^{51}Cr enriched material using liquid-liquid extraction of irradiated ammonium chromate still took place with scale to about 250 mg amount of Cr(tmhd)₃ synthesis product. The amount of ammonium chromate itself (36 mg) and accordingly the activity (2 MBq) were very low compared to this. The liquid-liquid extraction did not cause major problems and the amount of ^{51}Cr in the enriched aqueous phase was about 80% of the irradiated ^{51}Cr . After synthesis mass and radiometric yields were about 90% of the theoretical yields and after purification by column chromatography about 80%.

As a next attempt, an order of magnitude larger amount of ammonium chromate (600 mg) was used and the amount of synthesis was decreased by an order of magnitude (50 mg). Afterwards, a second synthesis was carried out with a likewise large amount of ammonium chromate (about 230 mg, but with increased irradiation time and reduced synthesis amount (25 mg). In both experiments, the mass yield of Cr(tmhd)₃ after synthesis was significantly reduced. A lot of green substance was visible in the synthesis flask and hardly any lilac

Amount of irradiated ammonium chromate used in the liquid-liquid extraction	36 mg	601 mg	224 mg
Activity in aqueous fraction after liquid-liquid extraction	77.5%	70.0%	72.0%
Synthesis scaling	250 mg	50 mg	25 mg
Synthesis [mass yield]	97%	34.9%	38.8%
Synthesis [radiometric yield]	–	24.4%	22.5%
Column [mass yield]	76.1%	–	–
Column [radiometric yield]	78.4%	–	–

Table 5.1: Comparison of the different $\text{Cr}(\text{tmhd})_3$ synthesis with ^{51}Cr enriched material using liquid-liquid extraction of irradiated ammonium chromate with MIBK

product. Both the mass yield (about 30-40% of the theoretical yields) and the radiometric (about 20-25%) were significantly below the calculated theoretical yields and also very significantly below the previous experimental results. A gamma spectroscopic test measurement of the waste fractions (despite the different solvents and amount of content to the usual measurement method (see subsection 2.2.5) it was sufficient as rough estimate) after the chloroform extraction of the $\text{Cr}(\text{tmhd})_3$ synthesis confirmed that most of the remaining ^{51}Cr was in the ethanol water mixture. In Table 5.1 the mass and radiometric yields of the different synthesis are compared to each other. It can be seen that the liquid-liquid extraction works well even with larger amounts of ammonium chromate. But in combination of large amounts of ammonium chromate and using a down-scaled $\text{Cr}(\text{tmhd})_3$ synthesis the synthesis yield is reduced significantly.

One assumption for this reduced efficiency in the synthesis is the large amount of ammonium chloride that is produced as a by-product during the liquid-liquid extraction. After dissolving ammonium chromate in hydrochloric acid, the chromium is extracted in the form of chromic acid with MIBK, leaving behind ammonium and chloride ions. These could be detected after the extraction and also in the ethanol-water mixture after the synthesis. To confirm that the failure of the synthesis was due to the ammonium chloride and not to other causes, possibly arising as a by-product from irradiation, i.e. the use of irradiated ammonium chromate instead of inactive ammonium chromate, the entire procedure (liquid-liquid extraction and a down-scaled synthesis afterwards with the resulting aqueous fraction) was repeated with the same amounts of inactive ammonium chromate (225 mg). Again, ammonium chloride was detected and the synthesis yielded only about 30%. This confirms the hypothesis of ammonium chloride as an interference for the down-scaled $\text{Cr}(\text{tmhd})_3$ synthesis.

5.4 Conclusion and outlook

The application of ^{51}Cr enriched material performing a column-chromatographic step on irradiated $\text{Cr}(\text{tmhd})_3$ in a radiosynthesis of $\text{Cr}(\text{tmhd})_3$ worked very well (good agreement of mass yield and radiometric yield and comparable yields to chapter 3). Liquid-liquid extraction is also a suitable method to enrich the ^{51}Cr well. However, for larger activities and therefore substance amounts ever increasing amounts of ammonium chloride are present, which interfere with the down-scaled synthesis. To overcome this problems, it is suggested that a way should be sought to drive out the ammonium chloride after liquid-liquid extraction. One possibility would be oxidative destruction by boiling with nitric acid; future experiments should show whether this works.

6 Summary and outlook

The chemical separation of neutron-induced ^{51}Cr from neutron-irradiated bulk Cr-containing target materials allowed generation of higher specific activity ^{51}Cr labeled $\text{Cr}(\text{tmhd})_3$. The purification and analysis steps after $\text{Cr}(\text{tmhd})_3$ radiosynthesis with added irradiated material indicated that the ^{51}Cr was present in $\text{Cr}(\text{tmhd})_3$ form. ^{51}Cr specific activity in $\text{Cr}(\text{tmhd})_3$ could be increased by two orders of magnitude without major problems and with only slight adaptations to the synthesis procedure.

Chemical incorporation of neutron-induced ^{51}Cr into the radiosynthesis of $\text{Cr}(\text{tmhd})_3$ was demonstrated by purification using a combination of chromatography and recrystallization.

Chemical separation (enrichment) of neutron-induced ^{51}Cr from irradiated bulk Cr-containing target materials was possible from both target materials (ammonium chromate and $\text{Cr}(\text{tmhd})_3$). However, liquid-liquid extraction of irradiated ammonium chromate proved a more practical choice, due both to the ease of chemical separation and the yields achieved.

Application of the chemically separated neutron-induced ^{51}Cr enriched material to a $\text{Cr}(\text{tmhd})_3$ radiosynthesis worked very well from both separation methods. A disadvantage of the isotope enrichment using liquid-liquid extraction is that the synthesis may result in significantly reduced yields. Apparently, the large amount of ammonium chloride, a by-product of the liquid-liquid extraction, interferes with the ligand change reaction.

Elimination of ammonium chloride may be possible by oxidative destruction with concentrated nitric acid, thermal distraction under reduced pressure or ion exchange reactions. In the absence of ammonium chloride, the intrinsic limit of the ^{51}Cr enrichment process may be probed. However, this would require precise low level determination of Cr-content, possibly by neutron activation analysis.



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