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Status Report on Organo-metallic Beams at GANIL

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Abstract. Previous experiments with organo-metallic compounds like ferrocene, nickelocene and magnesocene showed that a pure spectrum must be obtained on the residual gas mass analyser before running successfully on the ion source. In collaboration with the chemistry department of the University of Caen, LCMT-ENSI Caen, the synthesis of these metallocene compounds has been studied to provide enriched isotopic compounds to GANIL's users. The chemical transformation yields were 90%, 80% and 43%, respectively.

Vanadocene, chromocene, cobaltocene and ruthenocene compounds have first been studied with a gas mass analyser and then successfully tested on the ECR 4M ion source at GANIL. Some 15 μA of 51 V^{11+} , 20 μA of 52 Cr^{11+} , 22 μA of 59 Co^{11+} , and 17 μA of 102 Ru^{11+} were achieved. The comparison between the results obtained on the gas mass analyser and the ion beams provided by the source has allowed us to validate this method of determining whether or not an organo-metallic compound could be a candidate for running on our ECR ion source. As the ECR ion sources are tuned and used alternately on the GANIL injectors, the available time for the tests is rare, so this method could be an alternative for the validation of new compounds.

Key words organo-metallic, ecris, mivoc

1 Introduction

The MIVOC (Metallic Ions from Volatile Compound) [1] method is routinely and successfully used at GANIL for the production of nickel and iron beams at high intensity. For 5 years, eight runs of two weeks with nickelocene or ferrocene compounds were achieved on the accelerator. The method is simpler to implement and the tuning of the ECR ion source is easier than with the oven method. Consequently higher intensities were easily reached, and moreover, the method gave better ionisation efficiencies because the gaseous organo-metallic molecular did not stick on the plasma chamber wall as fast as the metallic vapour coming from the oven. The majority of the experiments were carried out with natural commercial nickelocene for the production of $^{58} \text{Ni}$. However the physicists asked us for new beams, like $^{64} \text{Ni}$ or $^{26} \text{Mg}$, requiring enriched isotopes to get a suitable high intensity.

Thus a collaboration for the study of the synthesis of enriched compounds was established with a chemistry laboratory (LCMT) of the ENSI Caen. To date, the synthesis of three compounds, ferrocene, nickelocene and magnesocene, has been developed, tested on the ion source and then proposed to the GANIL's users. An enriched $^{58} \text{Fe}$ ferrocene compound has been synthesized and then successfully used for experiments. The main goals of these studies

were to develop a method adapted to the small quantities used in the source and to obtain a good yield of the chemical transformation. The gas mass analyser appeared very useful to characterise the samples and to predict the feasibility of a beam; we used a "Transpector" Gas Mass Analyser (GMA) from "LEYBOLD" which allows the measurements of the partial pressures up to the mass 200. The partial pressures of the metallocene molecule "X (C₅H₅)₂" or "XCp₂" or "bis-cyclopentadienyl X" and of its fragments "XCp", and "X" (metallic element) can be seen on the spectrum as well as the partial pressures of the main impurities: masses "18" (water) ; masses "66", "40" and "39" (hydrocarbon fragments e.g. pump oil, solvent,...); or "Cp" fragments. The evolution of the level of the impurities is compared with those of the metallocene. Usually we consider the ratio of the highest partial pressure representing the metallocene "XCp₂", "XCp" or "X" over the highest partial pressure representing the main impurity. Most of the time the ratio is below one at the beginning of the process, then grows gradually. The compound is operational after some hours when the ratio is better than 5. This method of characterisation was applied to other metallocene compounds before testing them on the ion source. We noticed that the GMA configuration and the set-up of the vacuum system must be unchanged to keep the measurements comparable. For example, the pump speed can affect the partial pressures spectrum and some kind of

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pressure gauges set on the way of the metallocene flow can decompose up to 60% of the compound.

2 Ferrocene and Nickelocene

In 1999 the MIVOC method was investigated as an alternative to the low ionization efficiency (1%), the low intensity (5 eμA of $^{58}\text{Ni}^{11+}$), and the bad reliability of the nickel beams obtained with our micro-oven. First tests have been achieved with ferrocene then nickelocene compounds. The compound was placed in a hermetic box called MIVOC chamber, which has a volume of 40 cm³ and allows a great evaporation surface around 10 cm². Most of the times it is filled up with 1 g of compound, and can operate at least 2 weeks. The evolution of the compound can be seen through a glass enclosing the box. The mivoc chamber is axially positioned, about 60 cm from the ECR plasma, and connected via a rough one-turn regulation valve. Nevertheless the mechanical motorisation of the valve offers an angular resolution better than 0.25°, and allows an accurate adjustment of the input flow. A new valve, PFEIFFER EVR116, electrically controlled, is now in operation on the ECR 4 ion source. Due to the toxicity of organo-metallic compounds, the output flow of all vacuum pumps is canalized through high density filters.

The ferrocene compound, $\text{Fe}(\text{C}_5\text{H}_5)_2$ or FeCp_2 , is orange coloured and stable enough to be conditioned in the mivoc chamber in air, then stored in an argon atmosphere. Intensities of 92 eμA of $^{56}\text{Fe}^{9+}$ and 30 eμA of $^{56}\text{Fe}^{13+}$ have been produced [2].

The colour of nickelocene compound, $\text{Ni}(\text{C}_5\text{H}_5)_2$ or NiCp_2 , must be dark green, or nearly black, for an optimal operation; a brown colour indicates a deterioration of the compound which is sensitive to air and to heat. The use of an argon glove box is recommended for handling. Some hours of purification in vacuum are necessary, particularly after a quick manipulation in air. This is done off-line with the GMA, looking at the partial pressures ratio “ $\text{NiC}_{10}\text{H}_{10}$ ” over “ H_2O ” until it reaches 5. The consumption of the nickelocene itself remains low, about some tenth of mg. An intensity of 40 eμA of $^{58}\text{Ni}^{11+}$ allowed to reach 770 W of beam power on target at 75 MeV/u. A consumption of 3 mg/h has been measured i.e. 0.63 mg/h for the isotope ^{58}Ni . The ionization efficiency of the source for ^{58}Ni was around 18%. Elsewhere we observed deterioration (brown colouration) of a synthesized compound stored in a mivoc chamber during one year. Storage in an argon atmosphere, in a cool place, and protected from UV could avoid this.

All the results have been obtained without mixing gas, with the 14.5 GHz ECR4M ion source. We observed repetitive micro sparks in the source extraction when running at the maximum intensity, but without any trouble for most of the experiments. Probably due to the presence of metallocene molecules in the extraction region, the frequency and the intensity of the sparks grow if the total beam intensity is beyond 2.5 eμA. Once helium was used to stabilise the beam, but with a decrease of the intensity. After running 2 or 3 weeks, the carbon contamination of the plasma chamber wall did not affect significantly the stability or the performances of the source. Nevertheless the plasma chamber is changed and cleaned after each run with organo-metallic compounds.

The development of the ferrocene synthesis was achieved in 2000, and then 200 mg of enriched (93%) metallic ^{58}Fe were used to produced 1.6 g of enriched compound. The yield of the transformation was more than 90%. The ECR 4M ion source delivered a stable beam of 35 eμA of $^{58}\text{Fe}^{8+}$ during 2 weeks with a consumption of 4 mg/h. The nickelocene synthesis, developed in 2004, used the same method as for the ferrocene, and is describe below. For that, we have selected a method initially reported by Sutornin [3] and Perevalona [4] which is based on a transmetallation reaction between NiCl_2 and magnesocène. The best yield reported by the author was 72 %. This reaction needs to synthesize NiCl_2 which is obtained quantitatively by reaction of metallic nickel with an aqueous solution of HCl. The sample is then heated under vacuum to get NiCl_2 without any traces of water. Then we used this nickel salt as a source of nickelocene. We optimised the conditions (volume of solvent, number of equivalent of magnesocene, purification). The best result is obtained by using a minimum amount of tetrahydrofurane as solvent (1,5 mL / mmol of NiCl_2), a slight excess of magnesocene (1,15 equivalent) and a purification by sublimation. For this synthesis a glove box is needed for the opening of the sublimator. The yield of this two step synthesis (from metallic nickel or iron) is included from 80 to 100 %.

The measurements of the partial pressures on the gas mass analyser was very useful to determine in a first approach the quality of different synthesized samples which were compared to the spectrum obtained with commercial compounds. A final test on the ion source showed that the tuning and the performances of a synthesized compound were as good as with the commercial one.

3 Magnesocene

As the request of the physicists was a high intensity magnesium beam with the isotope 26 Mg, we first

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decide to test the production with the natural commercial magnesocene, $Mg(C_5H_5)_2$ or $Mg(Cp)_2$, and then to study a method for the synthesis with an enriched isotope. About 840 mg of a white commercial compound were placed in the MIVOC chamber using an argon-filled box to avoid contact with air and moisture. It was indispensable with this pyrophoric compound which burns or decomposes (brown colour) in a few seconds with air. Then it was out-gassed for one hour with the GMA. The main impurity “66” decreased very quickly, and at the end the ratio “MgCp” over “66” was around 10. On ECR 4M ion source at 20 kV, only two hours were necessary to obtain a stable beam with intensities around 50 eμA for $^{24}Mg^{5+}$ and around 30 eμA for $^{24}Mg^{7+}$ [5]. It seems to be easier and more efficient, 24%, to produce medium charge states of magnesium beams with the MIVOC method than with the oven; nevertheless higher intensities were obtained on the higher charge states, Mg 8+ and Mg 9+, with the large capacity oven but with a ionization efficiency of 14%. Now at Ganil both methods are available on the ECRIS to deliver a high powerful magnesium beam of 3 kW for the experiments at the energy of 76 MeV/u.

The most widely used method for the preparation of magnesocene is based on the reaction of cyclopentadiene (vapor phase) with metallic magnesium at 500 to 600°C [6]. It must be pointed out that these drastic conditions are not always easy to handle. Therefore other methods using lower temperatures have been reported. For these methods, a catalyst, usually formed by a titanium [7] or vanadium [8] salt, is needed. It is worth mentioning that these methods using low temperature work up are always using an excess of magnesium. This aspect is not compatible with the synthesis of magnesocene started from an isotopic enriched magnesium sample. Therefore we have investigated another way based on a transmetallation reaction engaging sodium cyclopentadienyl in THF is added (2 to 2.2 equivalents) at room temperature. The solution is then heated at 60°C for 40 minutes. The volatiles are removed under vacuum, and the crude magnesocene is purified by sublimation (the sublimator needs to be open in a glove box). The way using the dibromoethane gave the best yields; despite our effort to get pure magnesocene, we observed that the magnesocene purified by this way still possess large

The magnesium salt is first obtained almost quantitatively by reaction of 200 mg of metallic magnesium with 1,2-dichloroethane or 1,2-dibromoethane. Then a commercial solution of sodium cyclopentadienyl in THF is added (2 to 2.2 equivalents) at room temperature. The solution is then heated at 60°C for 40 minutes. The volatiles are removed under vacuum, and the crude magnesocene is purified by sublimation (the sublimator needs to be open in a glove box). The way using the dibromoethane gave the best yields; despite our effort to get pure magnesocene, we observed that the magnesocene purified by this way still possess large

amount of THF that certainly form a complex with the metallic centre. Finally, the best yield obtained, based on the starting magnesium used, is 69 % (874 mg) of a magnesocene-THF complex.

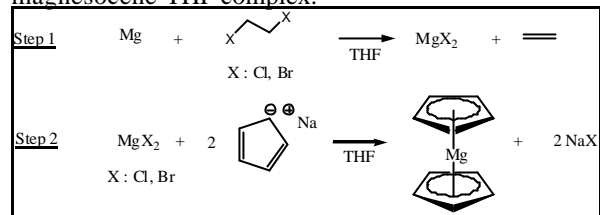


Fig.1 : Synthesis of magnesocene

The GMA revealed the composition of the sample. In a first time we only saw the impurities due to the THF (C_4H_8O) giving the mass “72” and its fragments like masses “71” or “42”, and tests on the ion source showed that it was impossible to get a magnesium beam if some THF impurity remains in the compound. Moreover, it could induce sparks and ionisation in the extraction region. In fact the partial pressure of $MgCp_2$ had to be greater than those of THF, by at least a factor of 5 as with the nickelocene for the water impurity. But if the same method is applied for out-gassing the compound with a high flux rate, both $MgCp_2$ and THF are pumping. The ratio “MgCp” (m=89) over mass “42” increases very slowly and when the purity is good a main part of the compound has been lost ! In this way we reached a global yield of synthesis of 19% in a few hours.

We also noticed that the spectrum with the partial pressures of the synthesized compound was drastically different according to the opening of the mivoc valve. Particularly at a very low flux rate, i.e. a total pressure of $3.2 \cdot 10^{-5}$ mbar, the ratio “MgCp” over “42” was lower than 0.01, around 0.05 at medium flux rate and equal to 0.7 at a high flux rate, i.e. a total pressure of $1.4 \cdot 10^{-4}$ mbar. As the THF had a vapour pressure a little bit higher than the magnesocene, its vapour held mainly the volume of the mivoc chamber. If the pumping applied to the mivoc chamber was low enough, the THF vapour pressure remains dominant; if not both THF and Magnesocene vapours feed the pumping flow. This observation was used to try the purification of the synthesized magnesocene compound. We operate at a medium flux rate (total pressure around $6 \cdot 10^{-5}$ mbar). At the beginning of the pumping, only the THF peaks are visible on the spectrum. The ratio “MgCp” over “42” was 0.25 after 15 hours, 0.5 after 55 hours and equal to 1 after 67 hours. From this moment the impurities decrease quickly, (fig.2) and a measurement done after 72 hours showed a ratio of 6.5, even at high flux rate (fig.3). Therefore we needed 3 days of pumping at medium flux rate for the purification of a synthesis sample leading to a global yield of the synthesis of 43%. Tests

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on the ion source gave results comparable to those with the commercial compound. One can expect to approach the chemical yield of 69% with a longer purification at a very low flux rate.

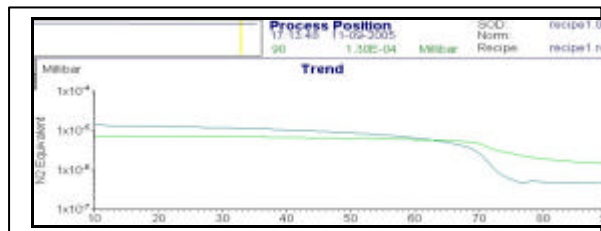


Fig. 2 : the last 17 hours of the magnesocene purification after 65h, THF(42) decreases faster than MgCp(89)

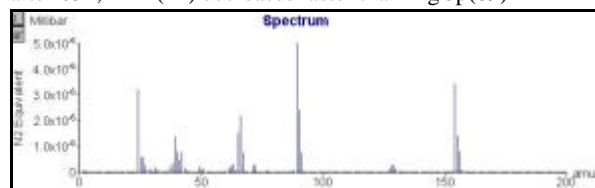


Fig. 3 : purified MgCp2 spectrum on gas mass analyzer

The residual gas mass analyser is a good way for a first approach to determine the feasibility of a beam with an organo-metallic compound on an ECR ion source. It allows to see and to measure the possible impurities and to decrease their rating with a controlled out-gassing of the compound.

4 Vanadocene, chromocene, cobaltocene and ruthenocene

The different advantages of the MIVOC method led us to carry on our tests about new metallocene beams, particularly with elements which seemed difficult or impossible to evaporate with the oven. Another objective was to find a quick method to characterize a sample and to test it on the ion source. The characterization has been done with the GMA in a short time, 2 hours per sample, and each test on ECR 4M went on for less than 12 hours. So the results have to be considered as a first approach of the feasibility of this kind of beam. The filling of the mivoc chambers has been done with the natural commercial forms in a glove box under argon. The out-gassing with the GMA gave indications about the properties of the compounds.

With vanadocene, $V(C_5H_5)_2$ or $V(Cp)_2$, the GMA spectrum showed water "18" and the mass "66" as main impurities which decrease in 30 mn and gave a final ratio pp "H2O" over Σ pp "VCp2, VCp, V" around 3%. A total pressure of $1.2 \cdot 10^{-4}$ mbar was obtained with the valve opened at $\frac{1}{4}$ turn. On the ion source we easily obtained a stable beam of 45 μA of $^{51}V^{7+}$, and then optimized on V^{10+} at 25 μA with

310 W of RF power and an extracted current of 1.6 mA.

With chromocene, $Cr(C_5H_5)_2$, similar observations were done on the GMA with a final level of 6% for water. A beam of $^{52}V^{8+} = 45 \mu A$ has been obtained with 250 W of RF power and an extracted current of 2.2 mA. As with vanadocene, water could be seen as H and O peaks on the CSD spectrum of the source, so we can think that higher intensities can be achieved after a longer out-gassing.

The cobaltocene appeared very pure on the GMA spectrum after some minutes, but the valve was fully open to have a final total pressure around $2 \cdot 10^{-4}$ mbar and a level of 1% for water. On the ion source we easily obtained an intensity of $^{59}Co^{9+}$ around 50 μA with 230 W of RF power and an extracted current of 2.1 mA.

The out-gassing of the ruthenocene, $Ru(C_5H_5)_2$ or $Ru(Cp)_2$, required a valve fully open to have a total pressure of $1.1 \cdot 10^{-4}$ mbar and a very slow decrease of the water partial pressure which remains at the same level as the ruthenocene after 1.5 hour. Let us notice that only the partial pressures of "Ru" ($m=102$) and "RuCp" ($m=167$) were available on the GMA. Nevertheless we tried running on the ion source. The intensities have been measured on the most abundant (32%) isotope, mass 102. A maximum intensity of 4 μA of $^{102}Ru^{9+}$ were produced at ambient temperature with the valve fully opened. Heating up to $80^\circ C$, the mivoc chamber with a warm air flow, we obtained 17 μA of $^{102}Ru^{11+}$ with only 125 W of RF power and an extracted current around 2.3 mA.

Seven beams from magnesium 24 to ruthenium 102 were produced with metallocene compounds. The observation of the CSD showed that these compounds are well adapted for the production of the medium charge state ion beams.

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