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MAGNETIC SYSTEM OF MARY SPECTROMETER: DESIGN AND IMPLEMENTATION

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The paper reports development of a dedicated magnetic field system for application in low field studies of chemical reactions involving paramagnetic intermediates. The relative advantages and shortcomings of traditional and yoke-free designs are addressed in the context of the target experiment, and the design considerations in terms of required field parameters and their practically attainable values are discussed. The details of calculation, construction, and testing of the actually built system are provided.

Keywords: MARY spectroscopy, low magnetic field, magnetic system, active shielding

1 INTRODUCTION

MARY (Magnetically Affected Reaction Yield) spectroscopy belongs to the family of the so-called spin chemistry techniques that are widely used in modern chemistry and biology to study reactions involving short-lived paramagnetic species: radicals, radical ions, excited states of molecules, *etc*. [1]. All these methods rely on application of external magnetic field in one form or another to affect the spins of unpaired electrons in the paramagnetic intermediates in a way that will eventually lead to certain observable results, *eg* to a change in the yield of reaction of recombination between two radicals, a change in the intensity of recombination fluorescence, or appreciable nuclear polarisation in the stable products of recombination. Sacrificing the high spectral resolution of the more traditional magnetoresonance techniques lice conventional Electron (ESR) or Nuclear (NMR) magnetic resonance, the methods of spin chemistry address their most serious limitation – the requirement to have rather high concentrations of relatively long-lived species that are studied. Thus, MARY spectroscope is routinely used to study radical ions living as short as several nanoseconds at stationary concentrations of $10^2 – 10^3$ species in the sample.

The method itself takes advantage of the resonance-like lines on the dependence of the intensity of recombination fluorescence from X-irradiated sample on external static magnetic field. The lines arise at zero and low (about 1 – 10 mT) magnetic fields due to coherent evolution of spins that are formed as correlated pairs upon ionisation of molecules, and are similar to Hanle signals used in high-sensitivity zero magnetic field indicators based on optically polarised alkali metal atoms. Since the signals are rather weak, usually field modulation with lock-in detection and symmetric passage through zero of the field is used. The details of the technique as applied in this laboratory can be found elsewhere [2]. The issues relevant for this work are that a sample with linear dimensions of about 1 cm should be placed in external static magnetic field that is cleanly swept from about “-10” to “+10” mT through zero, and there should be an X-ray tube (XRT) and a photomultiplier tube (PMT) as close to the sample as possible, both being rather sensitive to magnetic fields. The best possible homogeneity of the applied field is desired as always.

2 DESIGN CONSIDERATIONS

There are two common approaches that can possibly satisfy the formulated requirements, namely, a solenoid-type system with ferromagnetic core, and a yoke-free system of coils or rods along the lines of Helmholtz coils. The most important advantages of the core-type design are good confinement of the field, rather high current-to-field conversion ratio, and very good attainable field homogeneity with properly mage pole pieces. However, the most serious obstacle in the context of this project is the necessity to scan through zero of the field with maximum linearity – the most important field interval for the planned studies is fractions of millitesla around the zero. The produced field here will not be proportional to the current injected in the coils, which would require organising a feedback loop with a field sensor. However, it is difficult to find a sensor that will operate from practically zero field up to tens of millitesla with reasonable short time constant for stable feedback operation during field sweeping. The most common sensor types, fluxgates and Hall probes, are fine for portions of the range, but can not cover it all.

This serious problem is inherently eliminated in a yoke-free design. Here magnetic field is created by an arrangement of currents suspended in open space and is directly proportional to the injected currents, thus the currents themselves rather than magnetic field can be controlled. Furthermore, the fields created by different current elements add up linearly as vectors in space, so separate components of the field can be tailored individually and them superimposed as desired. The price

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for these advantages is much lower efficiency and difficulty of field confinement, as well as poorer field homogeneity. However, the positive aspects of the yoke-free design far outweigh its shortcomings here, so it was adopted as a basis for magnetic system for the new MARY spectrometer.

Based on our previous experience with MARY, the following requirements were formulated: magnetic field range from "-50" to "+50" mT, XRT not farther than 20 cm away from the sample, PMT as close to the sample as possible, magnetic field at the location of XRT/PMT not higher than 10 mT, opening for sample compartment at least 5 cm, external dimensions within 0.5 m, power consumption under 1 kW with water cooling. The system will not use any ferromagnetic elements such as magnetic screens for XRT/PMT that would impair field homogeneity. Practical limits for machining accuracy we set at ±0.1 mm, with thermal "breathing" of the distances in the system of the same order of magnitude, which implies practically attainable relative field homogeneity of about 10^{-4} – this figure was used in calculations. Since MARY lines in non-zero field are generally wider, the requirements for field homogeneity become more relaxed as the field is increased. The system will sweep field in one direction, further referred to as the "*Z*-axis". Stray fields in the perpendicular "*X*" and "*Y*" directions will be compensated by additional low-power coils. It is desirable to have a field sensor near the sample, which can be rather slow and will be used only for evaluation of the field by the operator.

3 SYSTEM LAYOUT

After evaluating several possibilities the following layout was chosen. The system will be a symmetric arrangement of coaxial coils along the *Z* axis, with XRT and PMT placed at the two opposite ends of the axis. The working region of the system is defined as a rather long cylinder 8 cm long by 1 cm diameter, which allows placing field sensor next to the sample after X-ray absorbers and still get the measure of the field at sample location. The sample compartment is a thick-walled "barrel" from aluminium alloy that provides the mechanical skeleton for rather heavy coils and attenuates low-frequency pick-up at mains frequency and its harmonics. Internal dimensions of the barrel (100 mm diameter and 140 mm length) provide ample room for placement of additional coils inside, wall thickness 20 mm.

The system is divided into two subsystems, further referred to as the "scanning" and the "power" systems. The scanning system consists of two pairs of coils and is designed form maximum relative field homogeneity (10^{-4}) in the working region. It creates continuously swept field from "-10" to "+10" mT. In the yoke-free arrangement field homogeneity improves, and efficiency drops as square of the linear dimensions, as the coil dimensions are increased. For this reason the coils were made as large as practical, and the created field range was deliberately limited to 10 mT, which still allows to perform complete experiments in the vicinity of zero field. The rate of field decay outside the working regions was left out of consideration, since the field there will never exceed a fraction of 10 mT.

The "power" system was designed from a different perspective, and consists of three pairs of coils. The system is required to produce field up to 40 mT, thus efficiency becomes an important issue. Due to rather high field its profile not only in the working region, but also outside it becomes critical. On the other hand, the system will be required to work outside the 10 mT range covered by the scanning system, where requirements for field homogeneity are less stringent. Thus a different compromise was reached. The power system is designed smaller than the scanning system and physically sits inside it and partially inside the barrel, which improves its efficiency at the price of certain loss of homogeneity. The system is designed with active shielding, similar to approaches used in pulsed NMR [3]. The innermost pair of coils is wired in the opposite polarity, which allows to significantly improve the steepness of field decay outside the working region. The system is be operated from a unipolar power supply and is stepped with field step 5 mT. The field of the opposite direction is created electronically reversing terminals at the power supply unit. The power system dissipates about 670 W at maximum field (40 mT), and the scanning system dissipates up to 200 W, so water cooling is used.

4 CALCULATIONS

The system was synthesised following the procedure described by Lugansky [4]. To find optimal coil parameters for producing the desired field profile in the region of optimisation the following functional was minimised

$$F = \int_{z_1}^{z_2} \left(\frac{B(z) - f(z)}{B(z_0)} \right)^2 dz \,, \tag{1}$$

where $f(z)$ is the field profile function and $B(z_0)$ is field at the reference point (centre). Integration is performed over the desired optimisation region only along the *Z* axis, since for a system of coaxial coils field homogeneity at the axis automatically leads to field homogeneity in the adjacent volume – the working region in our case. All calculations were carried out numerically in MATLAB environment, the integration was replaced by summing.

The procedure for optimisation of coils for the scanning system was as follows. First "thin", *ie* having point cross-section, coils were optimised for the working region only by varying three parameters for each pair of the system, current, radius, and inter-coil distance, using the textbook expression for field created by circular current at its axis. Then "thick" coils with finite rectangular cross-sections were placed with centres at the optimised positions and relative numbers of turns reflecting the optimised currents, and the cross - sections

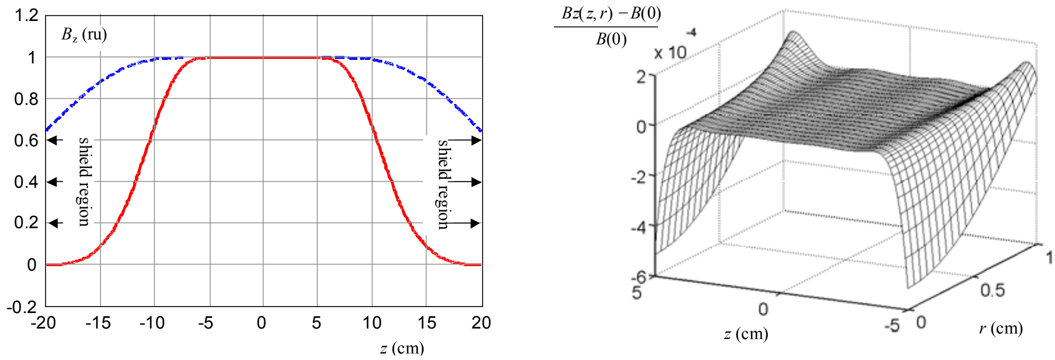

Fig. 1. Left: synthesised on-axis field profiles for the scanning (dashed line) and power (solid line) magnetic systems relative to field at the their centres (maximum 10 and 40 mT, respectively). The effect of active screening is clearly seen. The field at 15 cm from the centre (in the shield region) never exceeds 10 mT. The calculated relative RMS deviations of B_z on axis in the working region is 4.3x10^{-6} and 1.4x10^{-6} for the power and the scanning systems, respectively. Right: 3D plot of B_z field in the workings region (cylinder 8 cm x 1 cm)

and wire packing were optimised taking into account geometric restrictions.

This procedure was iterated until the sought results were obtained.The power system was synthesised in a similar way, but the range of optimisation was extended to include the shielding region, and the penalty function (1) was taken as the sum of two contributions of the form:

$$\delta = k\sum_{i=1}^{M}(B(z_i)-f\,(z_i))^2 \cdot \qquad (2)$$

where $f\,(z)\equiv 1$ and $k = k_1$ in the working region, and $f\,(z)\equiv 0$, $k = k_2 << k_1$ in the shield region and M was equal to 20-100. After optimising the on-axis field profiles the axial and radial components of the field in the entire cylinder of the working region were evaluated for both systems, and were found to be close to their on-axis values as expected. Fig. 1 shows the results of B_z field profile optimisation and its 3D plot.

Table 1. Optimal parameters: *Z*-displacement from centre (*Z*), radius (*r*), longitudinal (*ΔZ*) and radial (*Δr*) thickness, total current (*I*) and current density (*J*) for each pair of coils in the system in dimensionless units. All actual physical dimensions are obtained by multiplying by parameter *L* taken to be 0.05 m for this project, $I(A)=\frac{5\times10^6}{\pi}B(T)L(m)I_{opt}$, $J(Am^{-2})=\frac{5\times10^6}{\pi}\frac{B(T)}{L(m)}J_{opt}$

Coil Pair	z	r	Δz	Δr	I	J
Power System						
1	0.9727	2.3676	0.8372	0.9556	1.6000	1.9999
2	2.6294	2.0554	0.6118	0.6820	-0.8220	-2.0016
3	1.6776	1.0476	0.4508	0.4768	0.4307	2.0041
Scanning System						
1	0.8371	3.5251	0.4228	0.3844	1.2277	7.5540
2	2.8000	2.7556	0.4228	0.4488	1.4153	7.5483

The optimal coil parameters are collected in Table 1A schematic cross-section of the system and a photo of the physically built device are shown in Fig. 2.

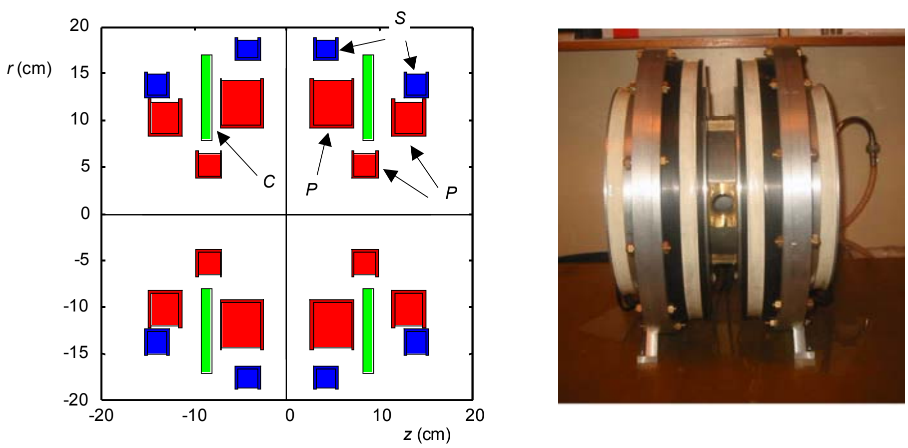

Fig. 2. Left: Schematic cross-section of the magnetic system shown to scale with three pairs of coils in the power system (P), two pairs of coils in the scanning system (S), and the cooling arrangement (C); Right: Photo of the device, outer dimensions slightly under 50 cm.

5 BUILDING AND TESTING

The designed system was built (see Fig. 2) and tested with its power supply. The coils were machined from aluminium alloy, wound with copper wire diameter 1.5 mm for the power and 1.4 mm for the scanning systems, and soaked with alumina-filled epoxy resin.

The carrying barrel was made so as to allow 0.5 mm margin for physical displacement of the coils using thin copper shims to fine tune the arrangement of coils.

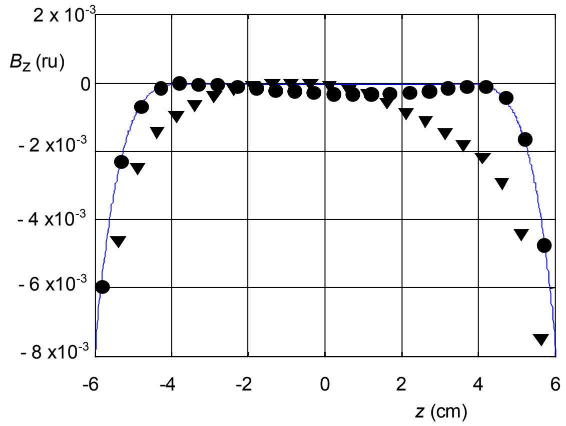

Fig. 3. Measured profile of the on-axis B_z field of the power system referenced to the field at the centre of the system. Solid line – theoretical calculations, filled circles – measurements for optimal (geometrical) parameters within assembling accuracy , filled triangles – measurements with all z-displacements of the (three pairs of) coils from centre uniformly reduced by 0.5 mm.

Magnetic field measurements were performed for each system separately using a modified Hall probe magnetometer SH1-8 with time constant increased to 15 seconds, sending rather high current (7 Amp) through the coils of the system connected in series. The coil dissipation in this regime was close to its rated value, and extended operation led to coil temperature rise of about 15˚C for ambient temperature 20˚C and tap water temperature 15˚C.

As an example Fig. 3 shows the measured B_z component at the axis of the power system as a function of displacement from its centre. Similar profiles were taken for both B_z and B_r components from both systems as functions of radial and axial displacement. The filled circles give the results of measurements for optimal coil geometry, and the filled triangles demonstrate the effect of uniformly reducing all z-displacements of the coils by 0.5 mm. The relative RMS deviations of the measured B_z values on axis in the working region was found to be about $1.5x10^{-4}$ for optimal coil geometry, as expected from the calculations, and about 10^{-3} for slightly distorted geometry, which demonstrates rather high sensitivity of the yoke-free design to geometry of the system.

It should be stressed that the geometry can (and have been) optimised to better field homogeneity, down to 10^{-6}, but the system becomes progressively more and more sensitive to minor deviations of parameters, so a more conservative target homogeneity of 10^{-4} was chosen, which produces much shallower minima with respect to optimisation parameters, and thus provides for a much more stable experimental device.

4 CONCLUSIONS

In the course of this project we have designed and built a yoke-free magnetic system for the new MARY spectrometer, which is optimised for creating rather low static homogeneous magnetic fields that can be cleanly swept through zero of the field. The built system creates magnetic field in the range from "-50" to "+50" mT in the cylindrical working region with length 8 cm and diameter 1 cm with relative homogeneity about 10^{-4} without using ferromagnetic elements or employing a field-sensing feedback loop. At the distance of 15 cm and farther away from the centre of the system magnetic field does not exceed 10 mT due to active screening, which allows putting magnetic field sensitive elements of the setup that close to the sample.

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