Drawing a different picture with pencil lead as matrix-assisted laser desorption/ionization matrix for fullerene derivatives

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Abstract

Inspired by reports on the use of pencil lead as a matrix-assisted laser desorption/ionization matrix, paving the way towards matrix-free matrix-assisted laser desorption/ionization, the present investigation evaluates its usage with organic fullerene derivatives. Currently, this class of compounds is best analysed using the electron transfer matrix trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB), which was employed as the standard here. The suitability of pencil lead was additionally compared to direct (i.e. no matrix) laser desorption/ionization-mass spectrometry. The use of (DCTB) was identified as the by far gentler method, producing spectra with abundant molecular ion signals and much reduced fragmentation. Analytically, pencil lead was found to be ineffective as a matrix, however, appears to be an extremely easy and inexpensive method for producing sodium and potassium adducts.

Keywords

Matrix-assisted laser desorption/ionization, pencil lead, (DCTB), sodium and potassium adducts, matrix, fullerene derivatives

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Introduction

The use of the material commonly referred to as ‘the matrix’ in matrix-assisted laser desorption/ionization (MALDI) is both a blessing and a curse. On the one hand, it delivers the softness for the overall desorption/ionization steps leading to ions that may otherwise decompose and on the other, the detection of low molecular weight compounds may be obscured by ions derived from the matrix itself. Moreover, the procedure by which matrix and sample are applied jointly to the target is often time-consuming and laborious which is not advantageous for the development of high-throughput methodologies. As a consequence, there has been increasing interest in modifications of MALDI that would still show its softness but without the use of the matrix. Such matrix-free desorption/ionization approaches are frequently categorized as surface-assisted laser desorption/ionization (SALDI), whereby a modified surface has properties that effectively provide conditions for overall soft desorption and ionization.^{1–6} The sample can be applied directly onto the surface and direct laser desorption/ionization (LDI) may be applied. The ease of sample preparation, however, often comes after what can be laborious and/or expensive procedures to modify the surface, such as the

etching of silicon with HF to produce porous silicon for desorption/ionization on silicon (DIOS).⁷

Langley and co-workers introduced an amazingly simple and inexpensive approach through the use of pencil lead,^{8,9} where the only surface modification is to draw a pencil over the stainless steel target plate. Pencil lead-MALDI combines two approaches within the modern development of MALDI. First, the ease of the target preparation provides an interesting addition to the repertoire of matrix-free MALDI or SALDI.^{1–6} Second, it features prominently amongst approaches that are applying carbon-based nano-materials such as graphite,^{10,11} fullerene derivatives,^{12,13} carbon nanotubes,¹⁴ –horns,¹⁵ as well as other carbon-based

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nanostructured materials^{5,6} and the carbon allotrope that became available most recently: graphene.¹⁶

The component of pencil lead assumed to provide the matrix effect is graphite, which has previously been successfully employed as a MALDI matrix.^{10,11} Issues arise, however, as it is typically difficult to apply to the target plate as well as to achieve an even reproducible surface coverage. Generally the softer the pencil, the more graphite it contains. There are many reasons why pencil lead would be a desirable matrix^{8,9} – its usage is safe, cheap with a quick and easy preparation, there are no solvent compatibility issues and the hydrophobic surface tends to help in producing a sweet spot.

In their initial paper,⁸ Langley and co-workers applied pencil lead to the analysis of various samples including peptides such as substance P, polymers, actinide metals such as uranium and terfenadine. For this study, a range of pencil grades were tested, ranging from 4H to 6B. It was found that 6B gave the best performance and this was assumed to be caused by it having the highest graphite content of all the pencils tested. Moreover, the softness of that particular pencil led to an easier application with more even coverage and appeared to offer a better reproducibility. A subsequent study⁹ tested a wider range of pencils on a selection of 50 small molecules, which included peptides, polymers, steroids and sugars. Contrary to the previous study,⁸ the 2B pencil was found to give the best results for the range of samples tested.

Pencil lead-MALDI has also been applied successfully to polymers, specifically to silyl hydride functionalised polystyrenes, which are particularly sensitive to the preparation methods commonly used in MALDI for polymers.¹⁷ For instance, the common use of dithranol as the matrix, with silver trifluoroacetate (AgTFA) as an additive, led to oxidation of the silane moiety. It was found that by using pencil lead and LiTFA, there were no side reactions, and the only adducts formed were lithium adducts. For pencil lead-MALDI of long alkyl esters of succinic and maleic acid, significant improvements in both reproducibility and sensitivity have been reported.¹⁸ Pencil lead-MALDI

analysis of model peptides has been compared with other matrix-free targets and gave only moderate performance.¹⁹ Also, the use of colloidal graphite led to improved results compared to the one of pencil lead for the analysis of low molecular weight analytes.²⁰

The fullerene derivatives under investigation are displayed in Figure 1. These methanofullerenes were produced by cyclopropanation^{21,22} and belong to a most versatile class of fullerene derivatives which gained tremendous importance as a means to induce structural changes and to modify material properties.²³ These adducts of C₆₀ with bis(alkoxycarbonyl)methylenes have been the subject to an earlier direct LDI study in which they produced intact molecular ions but also showed a considerable degree of fragmentation.²⁴ This makes them interesting candidates to test the performance of a MALDI matrix, which should enhance the molecular ion abundance and reduce fragmentation. We have used these analytes to establish the superiority of the trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) matrix in comparison with other organic matrix materials.²⁵ In addition to elucidating the electron transfer mechanism using the DCTB matrix,^{26,27} we have successfully employed DCTB to a variety of fullerene-related MALDI studies.^{28–32}

Experimental

All C₆₀ adducts (Figure 1) were synthesized according to literature procedures²¹ and purified by chromatographic means, so that individual compounds were free of any ligand attainment other than indicated by their formula.

All analytes were dissolved in toluene (Fisher Chemicals, 99% laboratory grade) at a 1 mg/ml concentration. A Fisherbrand Whirlimixer was used to ensure complete dissolution. DCTB (Fluka, Sigma-Aldrich, 99% HPLC grade) was prepared in a 10 mg/ml solution in toluene, which was added to the sample as required, typically in a 1:50 sample:DCTB molar ratio. 6B and 8B Staedtler branded Mars Lumograph pencils were

Figure 1. Structures of the fullerene derivatives under investigation with abbreviated names and nominal masses.

used throughout and were applied individually on the target spots. A pressure equivalent to writing was used to transfer pencil lead to the target plate, except in the experiments otherwise stated. The entire slide was held in an air stream to remove any loose pencil lead prior to sample application. Experiments in which higher pencil lead loadings were tested gave no other results.

The sample solutions were applied one drop at a time using a 1–10 μ l Bary mikroliterpipette and allowed to dry between applications. Typically 5 μ l of the solution was applied to each target spot.

For the DCTB experiments, the DCTB solution and sample were thoroughly mixed and applied together, typically 5 μ l of this solution was used per target spot. Mass spectra were acquired with a Bruker Ultraflex III. This MALDI-ToF (time-of-flight) mass spectrometer comes equipped with a SmartBeamTM laser which operates at 355 nm, with a repetition rate of between 1 and 200 Hz. Spectra were exported from the Bruker FlexAnalysis software for presentation purposes into the Origin software package.

Results and discussion

The adduct of C_{60} with bis(isopropoxycarbonyl)methylene (Figure 1) will be referred to in the following as **iso** and the corresponding adducts with one, two and three

bis(ethoxycarbonyl)-methylene ligands as **mono**, **bis** and **tris**, respectively. All four investigated methanofullerenes showed a similar behaviour under (MA)LDI conditions. In most experiments, **iso** was used because it is the most labile derivative of the four, which makes it the ideal candidate to test the softness of a method. However, to introduce the typical appearance of the pencil lead-MALDI spectra, **bis** was used as the analyte in Figure 2, as it can decompose not only into C_{60} but also into the mono-ligated species.

Figure 2 compares two pencil lead-MALDI spectra of **bis** using 6B (Figure 2(a)) and 8B pencil (Figure 2(b)). The spectra were obtained at a laser fluence adjusted to produce spectra with an overall high signal-to-noise ratio, rather than adjusting at the threshold of ion formation. Both spectra show extensive fragmentation leading to C_{60}^+ as the dominant peak at m/z 720. There are also $[C_{61}H]^+$ fragment ions at m/z 733 and to a lesser extent a signal that would correspond with the mass of **mono** is observed at m/z 878. As all the compounds were carefully purified prior to the experiment, there can be no doubt that the signals relating to C_{60} and **mono** are caused by fragmentation of **bis**. However, there is also formation of the molecular ion at m/z 1036 and as reported a typical feature in previous pencil lead-MALDI research, the quasi-molecular ions are abundantly formed as the

Figure 2. Pencil lead-MALDI mass spectra of **bis** applying (a) 6B pencil and (b) 8B pencil. Top line – full m/z range measured, bottom line – from m/z 700–1100.

Figure 3. Mass spectra of **iso** obtained at 8% laser fluence using (a) LDI, (b) DCTB-MALDI, (c) 6B pencil lead-MALDI and (d) 8B pencil lead-MALDI.

result of sodium and potassium addition to the intact compound. 6B pencil lead-MALDI (Figure 2(a)) shows the sodiated molecular ion peak as the most intense of the three at m/z 1059. Utilising the 8B pencil (Figure 2(b)), the potassium peak at m/z 39 dominates the spectrum. Direct comparison of the ion abundances in both spectra reveals how much more abundant the potassium production is from the 8B pencil with approx. 32,000 counts compared to 6B with 6000 counts. However, the 6B pencil appears to produce more analyte-derived ions (that is C_{60} -containing) than 8B.

In terms of matrix protection, pencil lead does not appear to offer any. In fact, the pencil lead-MALDI spectra are very similar in appearance to those obtained using direct LDI (see below). This was the case for all four fullerene derivatives analysed. When this method is compared to spectra obtained using DCTB as a matrix for MALDI-mass spectrometry (MS) (see below), it becomes apparent that DCTB offers a far superior protection for this class of compounds. However, pencil lead appears to aid ionization through the addition of sodium and potassium.

The sodiated and potassiated quasi-molecular ions clearly originate from the presence of pencil lead on the target, as the result of Na^+ and K^+ attachment to the neutral molecule. All other non-metallated ions, such as C_{60}^+ , the **mono** $^+$ fragment ion and the **bis** $^+$ radical cation can be assumed to result from direct LDI. This can be straightforwardly based on the close

similarity of the direct LDI mass spectra and those obtained by pencil lead-MALDI. However, we cannot rule out contributions from electron transfer with ions derived from the pencil lead. The metallated quasi-molecular ions are not likely to contribute (through fragmentation) to any of the non-metallated ions, because of the low ionization potential of the alkali cations preventing charge transfer reactions. Unfortunately this assumption could not be checked in LIFT (MS/MS following pencil lead-MALDI) experiments of the molecular and quasi-molecular ions, as these were always too low abundant to perform such experiments.

Finally, the malonate ligand is confirmed as the location of the Na^+/K^+ attachment, as pure C_{60} did not show signs of metalation in pencil lead-MALDI.

To thoroughly compare the performance of pencil lead-MALDI with DCTB-MALDI and direct LDI, the **iso** compound was analysed with each of those methods in the course of one session (using one target plate for all four methods), to negate fluctuations in machine performance. A series of spectra was obtained for each of the methods over a range of increasing laser fluences. The laser fluence is expressed here as an arbitrary unit in percent and ranged from 4 to 24%, at 4% increments. Below 4%, it was difficult to obtain a signal for any method and above 24%, the spectra did not alter much with higher laser fluences.

Figure 3 displays the analysis of **iso** by direct LDI (Figure 3(a)), DCTB-MALDI (Figure 3(b)) and pencil

Figure 4. Mass spectra of **iso** obtained at 16% laser fluence using (a) LDI, (b) DCTB-MALDI, (c) 6B pencil lead-MALDI and (d) 8B pencil lead-MALDI.

lead-MALDI with 6B (Figure 3(c)) and 8B pencil (Figure 3(d)) at 8% laser fluence, the lowest fluence at which ions could be detected at all by one of the methods.

The y-axis displays actual intensities (counts), rather than relative intensities as percentages normalized to the most dominant peak. This allows for direct comparison between each method. In the LDI (Figure 3(a)), 6B (Figure 3(c)) and 8B (Figure 3(d)) pencil spectra, the peaks are not higher than 20 counts. Comparison to the DCTB-MALDI spectrum (Figure 3(b)), where the true molecular ion peak of **iso** is obtained at a value of approximately 19,000 counts, shows the effectiveness of the DCTB-MALDI performance. DCTB produces the molecular ion peak at very low laser fluences, thus reduces the threshold for ionization dramatically.

Figure 4 reveals that the onset of the ion formation for the LDI (Figure 4(a)), 6B (Figure 4(c)) and 8B pencil lead (Figure 4(d)) conditions coincides with a laser fluence of 16%. The only analyte-derived ions with peaks at m/z 720 and m/z 733 are fragment ions as previously identified. Fragment ions may either arise from complete decomposition of directly ionised **iso** or through ionisation of fragments that result from decomposition of neutral **iso**. In any case, these ions indicate that fairly drastic conditions prevail. In the DCTB-MALDI spectrum (Figure 4(b)), the molecular ion is still the base peak, although additional

signals appear. The peaks at lower masses than m/z 906 may result from fragmentation (besides those derived from the matrix) and signals at higher mass can be attributed to the addition of DCTB to the analyte molecule. However, important is, that the fragmentation down to $C_{60}^{+•}$ is still rather minute with the molecular analyte ion representing the most abundant peak.

With the further increase in laser fluence to 20% (Figure 5), low abundant peaks due to the radical cation and the sodiated and potassiated analyte molecule start to appear in the pencil lead-MALDI spectra (Figure 5(c) and (d)). These peaks are much lower in intensity when compared to the fragmentation peaks. The LDI mass spectrum (Figure 5(a)) is still only producing fragmentation peaks. For the DCTB-MALDI mass spectrum (Figure 5(b)), although the matrix and fragmentation peaks gain in abundance, the molecular ion peak is still the dominant signal. The overall ion abundance with DCTB-MALDI is orders of magnitude larger than with the other methods, which demonstrates the enhanced efficiency of desorption and soft ion formation of this approach.

With regard to the use of pencil lead as a matrix for the analysis of derivatised fullerenes, the present experiments have demonstrated that it is an unsuitable replacement for the current standard matrix DCTB. The formation of quasi-molecular ions is observed in the form of sodium and potassium adducts to

Figure 5. Mass spectra of **iso** obtained at 20% laser fluence using (a) LDI, (b) DCTB-MALDI, (c) 6B pencil lead-MALDI and (d) 8B pencil lead-MALDI.

the analyte. However, the formation of such quasi-molecular ions occurs at such enhanced laser fluences that severe fragmentation is always observed as well. There is also some molecular ion present, however, the production of which is rather minute. Fragmentation is already abundantly observed at lower laser fluences than needed to observe the quasi-molecular ions. Therefore, a large fraction of the fragmentation may be caused by direct laser activation of analyte that remains unprotected through the pencil lead matrix. DCTB comes out as a far superior matrix, producing a molecular ion peak at low laser fluences, with much reduced or no fragmentation at all. LDI is the worst performing method of the four in terms of molecular ion formation.

Fullerene derivatization is often unspecific leading to multiple addition of ligands to C_{60} . A quick and reliable method to probe the product distribution is therefore desirable. In this context, pencil lead-MALDI was tested for the analysis of a 1:1:1 equi-molecular mix of **mono**, **bis** and **tris**, simulating a raw product following synthesis. The resulting spectra are shown in Figure 6 using 6B and 8B pencil. Certainly, since the performance of pencil lead-MALDI for the analysis of the isolated compound is rather poor, one cannot expect surprises for the analysis of a mixture.

But the outcome is even worse than expected. First, the huge signal for C_{60} is caused by extensive

fragmentation. Second, the ratios of sodium and potassium addition are different between the compounds – apparently random. **Mono** appears to not form a great number of either sodium or potassium adducts. On 8B pencil, **bis** shows the cation radical as the most abundant of the molecular ions (Figure 6(b)), yet it is the sodium adduct that is the most intense on 6B (Figure 6(a)). The most intense molecular ion for **tris** is the sodium adduct on both types of pencil, with a massive increase in the formation of the potassium adduct on 8B pencil (Figure 6(b)). Evidently, the spectra reflect the severe dissociation caused by direct LDI of the compounds with pencil lead failing to protect. Moreover, the different desorption efficiencies of the compounds may contribute as well as the fact that the malonate groups will statistically prefer the metal cation attainment in the order **tris** > **bis** > **mono**.

Conclusion

Pencil lead has been shown to be an unsatisfactory matrix for fullerenes and their derivatives, especially when compared to the benchmark of DCTB-MALDI. There is extensive fragmentation and the production of the molecular ion peak is commonly of low intensity. In general, higher laser fluences are needed than in DCTB-MALDI to produce any ions. Analytically valuable is

Figure 6. Mass spectra of **mono: bis: tris** in a 1:1:1 ratio, analysed by (a) 6B pencil lead-MALDI and (b) 8B pencil lead-MALDI. Top line displays the full m/z range of spectrum. The bottom line displays the molecular ion m/z range.

the addition of sodium and potassium cations to analytes with heteroatoms. This could be used for identification, but also can be useful as a means to produce such adducts for further experiments. The difference between 6B and 8B pencil was not pronounced in terms of matrix performance, however, 8B spectra produced higher quantities of potassium addition. Use of the 8B pencil did also seem to hinder ion production occasionally, with often lower abundance of analyte-derived ions and resulting in lower quality spectra overall.

In summary, pencil lead-MALDI does not match the quality of DCTB-MALDI regarding softness, cleanliness of spectra and sensitivity, but could have its merits as a facile approach to generate sodium and potassium adducts of structurally suited fullerene derivatives.

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Dedication

This article is dedicated to Prof. Peter J Derrick for the time at Warwick and beyond.

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