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COMBUSTÃO INICIADA POR MICRO-ONDAS EM FRASCOS DESCARTÁVEIS PARA DETERMINAÇÃO DE NÍQUEL E LANTÂNIO EM NANOTUBOS DE CARBONO POR TÉCNICAS ESPECTROMÉTRICAS

Santa Maria, RS
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Tese apresentada ao Programa de Pós-Graduação em Química, Área de concentração Química Analítica, da Universidade Federal de Santa Maria (UFSM, RS), como requisito parcial para obtenção do título de **Doutor em Ciências**.

Orientador: Prof. Dr. Fábio Andrei Duarte

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Neste trabalho, foi proposto o uso de combustão iniciada por micro-ondas em frascos descartáveis (MIC-DV) para a decomposição de nanotubos de carbono (CNT) e posterior determinação de Ni e La empregando colorimetria (para Ni) e a espectrometria de emissão óptica com plasma indutivamente acoplado (ICP-OES, para La). Os resultados estão divididos em dois manuscritos, sendo o primeiro com enfoque na decomposição de CNT por MIC-DV para posterior determinação colorimétrica utilizando um smartphone acoplado a uma USB vídeo câmera (UVC), inserida em uma câmara feita em impressão 3D (caracterizado como um *smartphone-based camera*, SBC). O segundo manuscrito tem como objetivo a decomposição de CNT por MIC-DV para posterior determinação de La por ICP-OES. Foram usadas duas amostras de CNT (parede múltipla), adquiridas no comercio nacional. Para obtenção dos valores de referência, foram empregados como métodos de preparo de amostra a decomposição assistida por radiação micro-ondas (MAD) e a combustão iniciada por micro-ondas (MIC). Como técnica de detecção de referência foi utilizada a ICP-OES. Para obtenção das melhores condições de operação do método de MIC-DV proposto, foi avaliada a influência de parâmetros como massa de amostra, volume e concentração da solução absorvedora e pressão aplicada no frasco de combustão. Os digeridos empregando a MIC-DV foram compatíveis com a técnica de determinação ICP-OES para Ni e La. Os resultados descritos no primeiro manuscrito demonstram que o método proposto (MIC-DV/SBC) apresentou resultados com boa concordância com o método de referência, variando entre 96 e 104%. No segundo manuscrito, os resultados para a determinação de La pelo método proposto (MIC-DV/ICP-OES) também apresentaram boa concordância com o método de referência, variando entre 92 e 99%. Os limites de quantificação no método proposto para determinação de Ni (MIC-DV/SBC) e La (MIC-DV/ICP-OES) foram de 115 e 3,5 µg g^{-1}, respectivamente. Além disso, o desempenho dos métodos propostos frente aos princípios da química analítica verde (GAC) foram avaliados utilizando a química analítica branca (*White Analytical Chemistry* – WAC). Quando comparado aos métodos de referência, foi possível observar que empregando a MIC-DV é possível obter uma redução significativa do volume de resíduo gerado. Além disso, os métodos propostos destacam-se quanto ao baixo custo e o excelente desempenho analítico apresentados. Sendo assim, eles podem ser caracterizados como uma alternativa adequada para aplicação em análises de rotina, devido ao baixo custo, frequência de análise, simplicidade e, principalmente, por estarem de acordo com os princípios da GAC.

Palavras-chave: Nanotubos de carbono. Níquel. Lantânio. MIC-DV. Smartphone. Colorimetria. ICP-OES.

ABSTRACT

MICROWAVE-INDUCED COMBUSTION IN DISPOSABLE VESSELS TO DETERMINE NICKEL AND LANTHANUM IN CARBON NANOTUBES USING SPECTROMETRIC TECHNIQUES

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In this work, the use of microwave-induced combustion in disposable vessels (MIC-DV) was proposed for the digestion of carbon nanotubes (CNT) and subsequent determination of Ni and La using colorimetry (for Ni) and inductively coupled plasma optical emission spectrometry (ICP-OES, for La). The results were separated in two manuscripts, where the first one focused on the digestion of CNT by MIC-DV for subsequent colorimetric Ni determination using a smartphone coupled to a USB video camera (UVC) inserted into a camera manufactured in a 3D printer (characterized as a smartphone-based method, SBC). The second manuscript purposes to CNT digestion by MIC-DV for determination of La by ICP-OES. Two CNT samples (multiple wall) were used and acquired in the national market. The reference values were obtained by microwave-assisted digestion (MAD) and microwave-induced combustion (MIC) were used as sample preparation methods. ICP-OES was used as reference detection technique. The best operating conditions for the proposed MIC-DV method were achieved evaluating the influence sample mass, volume and concentration of the absorber solution and pressure applied for the combustion flask. The digests from MIC-DV were compatible with the ICP-OES determination technique for Ni and La. The results obtained in the first manuscript evidenced that the proposed method (MIC-DV/SBC) presented results with good agreement with the reference method, ranging from 96 to 104%. In the second manuscript, the results for La determination by the proposed method (MIC-DV/ICP-OES) also showed good agreement with the reference method, ranging from 92 and 99%. The limits of quantification for the determination of Ni (MIC-DV/SBC) and La (MIC-DV/ICP-OES) were 115 and 3.5 $\mu g\ g^{-1}$, respectively. In addition, the performance of the proposed methods against the principles of green analytical chemistry (GAC) were evaluated using white analytical chemistry (White Analytical Chemistry - WAC) metric. When compared to the reference methods, it was possible to observe that using the MIC-DV it is possible to obtain a significant reduction in the volume of waste generated. In addition, the proposed methods stand out for their low cost and excellent analytical performance. Therefore, they can be characterized as a suitable alternative for application in routine analysis, due to the low cost, frequency of analysis, simplicity and, mainly, for being in agreement with the principles of GAC.

Keywords: Carbon nanotubes. Nickel. Lanthanum. MIC-DV. Smartphone. Colorimetry. ICP-OES.

SUMÁRIO

1 INTRODUÇÃO

Um dos grandes desafios da química é o desenvolvimento de métodos de preparo de amostra que vão ao encontro dos princípios da química analítica verde (GAC, do inglês *green analytical chemistry*) (TOBISZEWSKI, 2016). A maioria dos métodos oficiais de preparo de amostra contidos em compêndios nacionais ou internacionais para o controle de qualidade, seja de produtos alimentícios, químicos ou farmacêuticos, fazem uso de elevados volumes de solventes e reagentes (ARMENTA; GARRIGUES; DE LA GUARDIA, 2015). Além disso, são requeridas várias etapas para o preparo de amostra, tornando o método moroso e suscetível a erros, com impacto na precisão e exatidão dos resultados.

De acordo com os princípios da GAC, se faz necessária a utilização de solventes menos tóxicos ou até a eliminação destes, bem como a redução do uso de reagentes e outras substâncias químicas (TOBISZEWSKI, 2016; KIRCHOFF, 2003). Ademais, é necessário o desenvolvimento de métodos que possibilitem a miniaturização e a integração de processos empregando um único frasco de reação (MELCHERT; REIS; ROCHA, 2012; GALUSZKA; MIGASZEWSKI; NAMIEŚNIK, 2013). Cabe destacar, que a maioria dos métodos empregados em química analítica fazem uso de equipamentos com elevado custo. Deste modo, é cada vez mais necessário desenvolver métodos de preparo de amostra que sejam de baixo custo e simples operação, que possam ser aplicados em grande escala, possibilitando a conversão do analito em uma forma adequada para ser quantificado pela técnica instrumental escolhida.

Recentemente, Duarte e colaboradores (2020) desenvolveram um método de preparo de amostra, a combustão iniciada por micro-ondas em frascos descartáveis (MIC-DV, do inglês *microwave-induced combustion in disposable vessels*). O método de MIC-DV consiste na utilização de um forno micro-ondas doméstico e frascos de polipropileno descartáveis. A MIC-DV permite a redução do volume de reagentes empregados, bem como o preparo de amostra e a quantificação dos analitos poderem ser feitas no mesmo frasco reacional, seguindo o princípio do frasco único, o que também vai ao encontro dos princípios da GAC de integração e miniaturização de processos.

Nos últimos anos, combinado ao preparo de amostra, o desenvolvimento de técnicas de quantificação que possibilitem a realização de análises químicas com alta precisão, exatidão e baixo custo também tem ganho grande destaque. Neste contexto, o emprego de dispositivos móveis vem sendo proposto como uma técnica emergente, que

permite a realização de análises químicas com alta precisão e baixo custo operacional, além de possibilitar a realização de análises a campo com resultados rápidos (HONG; CHANG, 2014). As técnicas de análise de imagem digitais (DIA, do inglês *Digital Image Analysis*) ou métodos digitais baseados em imagens (DIB, do inglês *Digital Image-Based*) têm sido empregados em análises quantitativas na química analítica devido ao baixo custo da técnica (LYRA *et al*., 2014). Nesta estratégia, dispositivos para captura de imagens digitais comuns, tais como câmeras, webcams, scanners e telefones celulares com uma câmera embutida têm sido usados para registrar imagens de reações colorimétricas (BENEDETTI *et al*., 2015) e entalpimétricas (BARIN, *et al*., 2015), onde é identificada a variação da intensidade de cor e de entalpia de uma reação, respectivamente.

Neste contexto de desenvolvimento de métodos analíticos sustentáveis, de baixo custo e portáteis, o presente trabalho propõe o emprego da MIC-DV como método de preparo de amostra, combinado ao uso de smartphone para posterior determinação de Ni e La em nanotubos de carbono (CNT).

2 REVISÃO DA LITERATURA

Neste capítulo será realizada uma revisão da literatura onde serão abordados aspectos gerais sobre os princípios da química analítica verde, bem como os métodos de preparo de amostra que fazem uso de tecnologias que vão ao encontro destes princípios. Em seguida, será abordado o uso de dispositivos portáteis como técnica para determinação elementar.

2.1   QUÍMICA ANALÍTICA VERDE

A Química Verde, tornou-se uma ferramenta para avaliar as práticas sustentáveis em laboratórios e indústrias, garantindo não só a redução do impacto ambiental gerado, mas também a segurança do operador (ANASTAS, 1999). Neste contexto, Anastas e Warner (1998) formularam os 12 princípios da química verde, com ênfase na descrição dos princípios para implementar sínteses químicas "verdes" em escala tecnológica, sendo estes princípios estruturados com diretrizes para atender a área da química sintética. Entretanto, alguns conceitos importantes na química analítica não foram abordados nos 12 princípios da química verde. Além disso, alguns dos conceitos abordados, como a economia de átomos, é insuficiente para a química analítica (GAŁUSZKA; MIGASZEWSKI; NAMIEŚNIK, 2013).

Neste contexto, tendo em vista que o desenvolvimento de métodos analíticos passou a ser uma das áreas mais ativas junto a pesquisa e desenvolvimento de métodos que fossem ao encontro dos princípios da química verde, Gałuszka e colaboradores (2013), sugeriram os 12 princípios da GAC. Para isso, quatro princípios da química verde foram mantidos e oitos novos princípios foram incorporados, visando abranger os conceitos mais importante da química analítica. Neste âmbito, a GAC surgiu como uma extensão da química verde, com enfoque no papel do químico analítico em tornar metodologias e práticas laboratoriais mais "ambientalmente corretas".

Os 12 princípios da GAC abordam como diretrizes, *i)* o uso de técnicas de análise diretas; *ii)* redução do volume e massa de amostra; *iii)* análises *in situ*; *iv)* economia de energia e redução do volume de reagentes com a integração de processos; *v)* miniaturização e automatização de métodos; *vi)* remoção das etapas de derivatização; *vii)* redução de resíduos; *viii)* desenvolvimento de métodos para determinação de multi-analitos e/ou multi-parâmetros; *ix)* redução do gasto de energia; *x)* uso de reagentes obtidos a partir de fontes renováveis; *xi)* substituição e/ou eliminação de reagentes tóxicos; *xii)* maior segurança ao operador (GAŁUSZKA; MIGASZEWSKI; NAMIEŚNIK, 2013). Desta forma, torna-se necessário o desenvolvimento de novos métodos de preparo de amostra que vão ao encontro destes princípios. Cabe destacar que, a etapa de preparo de amostra é tida como uma das etapas mais morosas do processo de análise, além de envolver na maioria das vezes o uso de elevados volumes de reagentes, por vezes tóxicos.

Atualmente, no desenvolvimento de novos métodos de preparo de amostra que sigam os conceitos da GAC, têm-se observado a crescente aplicação da radiação micro-ondas. A radiação micro-ondas vem sendo amplamente aplicada no preparo de amostras de matrizes orgânicas, destacando-se como principais vantagens o uso de ácidos diluídos, redução do volume de reagente e resíduo gerado (BIZZI, *et al*., 2011(a); BIZZI, *et al*., 2011(b); PICOLOTO, *et al*., 2017; SAVIO; FIALHO; NÓBREGA; 2019; TARANTINO, *et al*., 2017). Além disso, é possível realizar a digestão seguida da recuperação dos ácidos digeridos, o que vai ao encontro dos princípios da química verde de reduzir e reutilizar (SAVIO; FIALHO; NÓBREGA; 2019). A radiação micro-ondas também tem sido aplicada para extração de compostos orgânicos, possibilitando a redução do uso de solventes tóxicos e a redução de gasto energético devido ao menor tempo de extração (FERREIRA, *et al*., 2019).

2.2   MÉTODOS DE PREPARO DE AMOSTRA

A maioria das técnicas de quantificação, com exceção da análise direta de amostras sólidas, requer a conversão do sólido para uma solução compatível com o sistema de detecção. Desta forma, a etapa de preparo de amostra tem por objetivo a conversão do analito em uma forma adequada para ser quantificado pela técnica escolhida (KRUG; ROCHA, 2019).

Considerando a diversidade de matrizes existentes e que necessitam ser analisadas, se faz necessário o desenvolvimento de novos métodos de preparo de amostra que sejam eficazes para diferentes tipos de amostra. De maneira simplificada, as amostras podem ser classificadas como orgânicas, quando a matriz é predominante de compostos orgânicos, ou inorgânicas, quando há baixo teor orgânico e predominância de compostos metálicos, óxidos e sais (KRUG; ROCHA, 2019). Uma classificação para os métodos de preparo de amostra é proposta por Knapp (1991), sendo eles decomposição por via úmida, combustão, fusão e piroidrólise. Dentre estes métodos, a decomposição por via úmida e os métodos de combustão tem são considerados como o estado da arte para o preparo de amostras, principalmente combinados à radiação micro-ondas (MÜLLER, *et al*., 2014).

A decomposição por via úmida pode ser feita em sistemas abertos ou fechados, embora sua eficiência frente ao uso de ácidos diluídos tenha sido demonstrada (BIZZI, *et al*., 2011(a); BIZZI, *et al*., 2011(b)), é rotineiramente realizada utilizando ácidos concentrados e sob aquecimento. O HNO_3 é principal ácido empregado na decomposição

por via úmida para oxidação da matéria orgânica, podendo ser utilizado aquecimento convencional ou por radiação micro-ondas (KRUG; ROCHA, 2019). Os sistemas de decomposição fechados apresentam vantagens sobre os sistemas abertos, devido a temperatura alcançada no sistema devido ao aumento do ponto de ebulição do ácido. Além disso, o aquecimento gerado pela ação das micro-ondas acelera o processo de decomposição, visto que a transferência de calor é favorecida quando comparado ao aquecimento convencional. (KRUG; ROCHA, 2019).

Os métodos de combustão também podem ser executados em sistemas abertos ou fechados, sendo o método de combustão empregando fornos do tipo mufla um dos sistemas abertos mais comumente empregado (MORTARI, *et al.*, 2010; GRINBERG, *et al.*, 2015). Como sistemas fechados de combustão, destacam-se o frasco de Schöniger, a bomba de combustão, a combustão iniciada por micro-ondas (MIC) e, mais recentemente, a combustão iniciada por micro-ondas em frascos descartáveis (MIC-DV).

Cabe destacar que, a escolha do método de preparo de amostra dependerá da natureza da amostra, do analito a ser determinado, assim como sua concentração, técnica de determinação e, por fim, da exatidão e precisão almejadas (ARRUDA; SANTELLI, 1997). Para o preparo de amostras de CNT e posterior determinação de contaminantes inorgânicos (MORTARI, *et al.*, 2010; GRINBERG, *et al.*, 2015; KRZYZANIAK, *et al.*, 2019) o uso de radiação micro-ondas na etapa de preparo de amostra têm apresentado grande potencial de aplicação. Neste contexto, a seguir, serão abordados brevemente os principais métodos de preparo de amostra que fazem uso da radiação micro-ondas.

2.2.1 Decomposição por via úmida assistida por radiação micro-ondas

As micro-ondas são ondas eletromagnéticas que possuem frequência na faixa de 300 a 300.000 MHz, com comprimento de onda que varia de 0,1 a 100 cm. A frequência de 2450 MHz é a mais utilizada em equipamentos domésticos e para uso em laboratório. Cabe destacar que, a principal diferença entre o aquecimento convencional e o aquecimento gerado pela irradiação com micro-ondas está na forma de transferência de energia, onde a radiação eletromagnética é absorvida e convertida em energia térmica (calor) (ARRUDA; SANTELLI, 1997).

O mecanismo de transferência de energia envolvido nas micro-ondas difere dos mecanismos convencionais de transferência de energia térmica (condução, convecção e irradiação). A aplicação desta energia faz com que ocorram movimentos das espécies

presentes na solução pela migração de íons e/ou rotação de dipolos, que são causadas pelo elevado número de vezes em que o campo eletromagnético oscila (FLORES, 2014). O aquecimento não é produzido por fonte externa de aquecimento, mas sim, pela interação entre as micro-ondas e as moléculas do sistema irradiado. Deste modo, é necessária a presença de moléculas com momento dipolar e/ou íons em solução para que ocorra o aquecimento (KRUG; ROCHA, 2019).

A decomposição em sistemas fechados assistida por radiação micro-ondas é uma alternativa aos sistemas de decomposição com aquecimento convencional. A decomposição por via úmida faz uso de ácidos concentrados, sendo o HNO_3 o principal ácido empregado para a decomposição da matéria orgânica, podendo o mesmo ser combinado junto a outros reagentes como, HCl, H_2SO_4 ou H_2O_2 (KRUG; ROCHA, 2019).

Na década de 90, iniciou-se a crescente aplicação da radiação micro-ondas na etapa de preparo de amostras. Isto ocorreu devido ao desenvolvimento de frascos a base de fluoropolímeros que possibilitaram a decomposição de amostras sob altas temperaturas e pressões e com baixos teores de contaminantes (KRUG; ROCHA, 2019). A decomposição de amostras em sistemas fechados permite uma melhor eficiência de decomposição quando comparado aos sistemas com aquecimento convencional, visto que a transferência de calor é favorecida (KRUG; ROCHA, 2019).

Nos sistemas de decomposição assistida por radiação micro-ondas, os frascos empregados devem ser transparentes à radiação, bem como resistir a altas pressões e temperaturas. Os materiais que tem sido mais utilizados são o politetrafluoroetileno (PTFE), o perfluoralcoxi (PFA) e o quartzo (KRUG; ROCHA, 2019). Como vantagens das técnicas que utilizam a radiação micro-ondas em sistema fechado para decomposição de amostras, pode-se citar o aumento da eficiência de decomposição em um menor tempo, uma vez que os sistemas suportam pressões elevadas, contribuindo para o aumento da temperatura na fase líquida, devido ao aumento do ponto de ebulição dos reagentes (FLORES, 2014). Além disso, uma maior segurança é garantida, uma vez que os sensores utilizados são capazes de controlar a pressão e a temperatura da mistura no momento da decomposição, além da potência irradiada em tempo real (ARRUDA; SANTELLI, 1997).

A decomposição de amostras por via úmida em sistema fechado assistido por radiação micro-ondas tem se mostrado um método de preparo de amostra eficiente, rápido e seguro. Aplicações para decomposição de amostras biológicas (BIZZI, *et al*., 2011(c); BIZZI, *et al*., 2014), botânicas (PARDINHO, *et al*., 2018), combustíveis (DRUZIAN, *et al*., 2016) e polímeros (PEREIRA, *et al*., 2016). Porém, para a decomposição de algumas

amostras, como os CNT, algumas dificuldades têm sido relatadas em decorrência da inércia química destes materiais. Desta forma, há uma limitação na massa de amostra empregada na decomposição, acarretando também no uso de maiores quantidades de reagentes e um maior tempo de decomposição (ANTES, *et al.*, 2010; LIM; BAIRI; FONG, 2017; KRZYZANIAK, *et al.*, 2019).

2.2.2 Métodos de combustão

O emprego dos métodos de decomposição por via úmida assistido por radiação micro-ondas pode não ser totalmente eficiente para algumas matrizes, acarretando assim na decomposição incompleta da amostra. Como alternativa, os métodos envolvendo reações de combustão tem apresentado bons resultados para o preparo de amostras orgânicas. De forma geral, os sistemas de combustão consistem na oxidação da matéria orgânica na presença de oxigênio, gerando como produtos principais CO_2 e H_2O. Para a retenção dos analitos liberados durante e após a reação de combustão, é empregada uma solução absorvedora adequada (geralmente ácida para metais e metaloides e alcalina para halogênios). (KRUG; ROCHA, 2019).

As reações de combustão podem ser realizadas em sistemas abertos ou fechados. A combustão por via seca em forno do tipo mufla é o sistema aberto mais simples empregado para a decomposição de amostras orgânicas. Neste método, a combustão da matéria orgânica ocorre na presença do oxigênio disponível no ar atmosférico (KRUG; ROCHA, 2019). A decomposição por via seca em forno do tipo mufla é um método relativamente simples e já foi empregada para decomposição de CNT para posterior determinação de contaminantes inorgânicos (MORTARI, *et al.*, 2010; GRINBERG, *et al.*, 2015). Porém, algumas desvantagens são apontadas para o uso deste tipo de sistema, como a perda de analitos na forma de espécies voláteis, a projeção da amostra, além da adsorção de analitos no recipiente de condicionamento da amostra. Outros métodos empregando sistema aberto com combustão iniciada por micro-ondas também podem ser utilizados, como o sistema dinâmico de combustão (Trace-O-Mat) e o sistema Wickbold (KRUG; ROCHA, 2019), porém devido a certa complexidade instrumental, têm sido pouco usados na atualidade.

Dentre os métodos de combustão empregando sistema fechado, destacam-se o frasco de Schöniger, a bomba de combustão e a combustão iniciada por micro-ondas (MIC). A principal vantagem destes sistemas é a diminuição de perdas de analitos na

forma de espécies voláteis, além de menores riscos de contaminação quando comparado aos sistemas abertos (KRUG; ROCHA, 2019). Com isso, tendo em vista as vantagens dos métodos de combustão em sistema fechado, este grupo será discutido com maiores detalhes.

2.2.2.1 Combustão com frasco de Schöniger

Como características ideais, os sistemas de decomposição devem ser de fácil operação, com instrumentação simples e garantir a oxidação completa de amostras orgânicas. Neste contexto, o frasco de combustão de Schöniger, conhecido também como frasco de combustão com oxigênio, foi desenvolvido para a decomposição de amostras orgânicas e posterior quantificação de elementos em baixas concentrações, de modo a garantir as características citadas acima (KRUG; ROCHA, 2019). De maneira geral, o método consiste em envolver a amostra em um papel com baixo teor de cinzas e suspendê-la em um suporte de platina para posterior inserção no frasco com atmosfera saturada de oxigênio, contendo uma solução absorvedora adequada para a absorção dos analitos. A ignição pode ser feita eletricamente ou com radiação infravermelha. Para garantir a completa vedação do frasco, ele é invertido para que a solução absorvedora auxilie na vedação da tampa. Após a combustão, o frasco é agitado manualmente para garantir completa absorção dos produtos de combustão (KRUG; ROCHA, 2019).

Os frascos de Schöniger, em sua maioria, são confeccionados em vidro borossilicato, podendo também ser de quartzo e policarbonato. O tamanho do frasco dependerá da massa de amostra a ser queimada, sendo uma limitação o volume de frasco disponível comercialmente, que possui volume não superior a 2 L e permite a queima de, no máximo, 50 mg de amostra (KRUG; ROCHA, 2019). O método de combustão em frasco de Schöniger foi utilizado para a decomposição de amostras orgânicas (FORBES; BOUND; WEST, 1979; TUCKERMAN, *et al*., 1959; GENG, *et al*., 2010), bem como amostras inorgânicas (GENG, *et al*., 2008). Este método apresenta como principais vantagens o baixo custo, rapidez na decomposição, baixo riscos de contaminação e de perdas de analitos na sua forma volátil (KRUG; ROCHA, 2019). Porém, algumas desvantagens são citadas na literatura, como a adsorção de analitos no suporte de platina, bem como a ausência da etapa de refluxo após a decomposição, bem como a massa de amostra a ser decomposta também é limitada neste sistema (GAWARGIOUS; BOULUS; FALTAOOS, 1976; FORBES; BOUND; WEST, 1979; GENG, *et al*., 2010).

2.2.2.2 Bomba de combustão

O sistema de preparo de amostra empregando a bomba de combustão consiste em um recipiente para decomposição, com volume interno de aproximadamente 300 mL. Ao interior do recipiente é adicionado um volume entre 5 e 10 mL de solução absorvedora adequada para absorção dos analitos. As amostras são inseridas na forma de comprimido, o qual é posicionado no copo de ignição em contato com dois eletrodos de platina para ignição. Após o fechamento do sistema, é realizada a pressurização com oxigênio, com pressões entre 20 e 30 atm. A ignição é realizada através do contato elétrico existente entre os dois eletrodos de platina e a amostra. Ao final da reação de combustão, o resfriamento do sistema pode ser acelerado realizando a submersão do mesmo em água ou em banho de gelo. Posterior a isso, é feita a abertura do frasco e a coleta do digerido (KRUG; ROCHA, 2019).

O sistema de bomba de combustão pode ser empregado principalmente para o preparo de amostras orgânicas. (LINDAHL; BISHOP, 1982; SOUZA, *et al*., 2002). A principal vantagem deste sistema está na massa de amostra relativamente alta que pode ser decomposta (podendo ser superior a 500 mg), bem como os baixos teores de carbono residual, quando comparado aos sistemas de decomposição por via úmida. Porém, algumas desvantagens são relatadas, como problemas de contaminação durante a decomposição devido o revestimento metálico do frasco reacional. Além disso, apresenta uma baixa frequência de processamento, podendo apenas uma amostra ser decomposta por vez, além da ausência da etapa de refluxo após a decomposição, o que pode afetar a recuperação dos analitos (KRUG; ROCHA, 2019).

2.2.2.3 Combustão iniciada por micro-ondas

O primeiro sistema de combustão iniciada por micro-ondas em sistema fechado foi proposto por Barin (2003). O sistema consistiu na utilização de um forno micro-ondas doméstico e frascos de PTFE empregando oxigênio líquido como fonte de O_2 para decomposição de fármacos. Posteriormente, um sistema de MIC comercial foi desenvolvido e aplicado para a digestão de materiais de referência certificado de fígado bovino, rim suíno e leite em pó, para posterior quantificação de Cd e Cu por

espectrometria de absorção atômica com forno de grafite (GF AAS) (FLORES, *et al*., 2004).

O sistema comercial da MIC consiste em um frasco de quartzo contendo um suporte interno confeccionado do mesmo material. A amostra é inserida no suporte, geralmente na forma de comprimido, sobre um papel filtro contendo uma solução iniciadora de combustão (geralmente NH_4NO_3). Ao frasco é adicionado um volume (não devendo ser inferior a 6 mL) de solução absorvedora adequada para absorção dos analitos. Posteriormente, é feito o fechamento e pressurização dos frascos com O_2, os quais são introduzidos na cavidade do forno de micro-ondas específico para uso em laboratório. Após a combustão, é possível realizar uma etapa de refluxo para garantir a absorção dos analitos, sendo esta etapa possível devido ao aquecimento da solução absorvedora que lixiviará pelas paredes do frasco e o suporte (FLORES, *et al*., 2004; FLORES, 2014; KRUG; ROCHA, 2019).

A MIC combina as vantagens do método de decomposição por via úmida assistida por radiação micro-ondas com as da combustão em sistemas fechados. As principais vantagens da MIC são a eficiência na decomposição de amostras orgânicas, mesmo as de difícil decomposição (FLORES, *et al*., 2004; PEREIRA, *et al*., 2016; PEREIRA, et a., 2015; PICOLOTO *et al*., 2019), bem como de matrizes inorgânicas. Além disso, podem ser empregadas soluções absorvedoras diluídas, reduzindo o gasto de reagentes e os riscos de contaminação. O método de MIC já foi aplicado para a decomposição de CNT e posterior determinação de Ni e La (MORTARI, *et al*., 2010. Assim como os demais métodos de preparo de amostras citados acima, na MIC, após a combustão, os digeridos são transferidos para frascos volumétricos e avolumados. Entretanto, esse procedimento acarreta a diluição do digerido e pode comprometer o limite de quantificação (LOQ), sendo uma desvantagem deste e da maioria dos métodos de decomposição disponíveis, estando em desacordo com um dos princípios da química verde, que são a integração e miniaturização de processos que pode ser atendido pelo princípio do frasco único. Além disso, o sistema comercial de MIC possui um custo relativamente alto de aquisição. Neste contexto, Duarte e colaboradores (2018) desenvolveram um sistema de MIC-DV, sendo o mesmo descrito a seguir.

2.2.2.4 Combustão iniciada por micro-ondas em frascos descartáveis

O método de MIC-DV foi proposto por WAECHTER (2017) para a decomposição de sangue empregando um forno de micro-ondas doméstico e frascos de polipropileno descartáveis. O sistema de MIC-DV combina as vantagens do método de MIC e possibilita que algumas desvantagens do sistema convencional sejam eliminadas, devido ao baixo custo de montagem do sistema, bem como a utilização do mesmo frasco empregado no preparo da amostra para a posterior etapa de quantificação, seguindo o princípio frasco único (DUARTE, *et al*., 2020).

O sistema de MIC consiste em um frasco de polipropileno de 50 mL, contendo um suporte interno confeccionado em quartzo. Assim como o sistema de MIC convencional, a amostra é inserida no suporte, geralmente na forma de comprimido e sobre um papel filtro contendo uma solução iniciadora de combustão (geralmente NH_4NO_3). Em seguida, o suporte é inserido no frasco reacional contendo 5 mL de solução absorvedora. Posteriormente, os frascos são purgados ou pressurizados com O_2 e os frascos são posicionados em um rotor metálico de alumínio. Em seguida, o rotor é posicionado na cavidade do forno micro-ondas e submetido ao programa de irradiação. Após a combustão, os frascos são retirados do rotor, agitados manualmente, abertos e, por fim, os suportes de quartzo são retirados e os digeridos estão prontos para a etapa de determinação (WAECHTER, 2017).

A seguir, serão abordadas as principais técnicas espectrométricas para quantificação elementar em química analítica, citando suas vantagens e desvantagens, com enfoque nas técnicas que serão empregadas neste trabalho.

2.3   TÉCNICAS ANALÍTICAS PARA A DETERMINAÇÃO ELEMENTAR EM CNT

Para a determinação de contaminantes inorgânicos em amostras de CNT, as principais técnicas analíticas que tem sido relatadas na literatura são as espectrométricas, destacando-se a espectrometria de emissão óptica com plasma indutivamente acoplado (ICP-OES, do inglês, *inductively coupled plasma optical emission spectrometry*) e a espectrometria de massa com plasma indutivamente acoplado (ICP-MS, do inglês, *inductively coupled plasma mass spectrometry*) (MELLO, *et al*., 2011; AVRAMESCU; RASMUSSEN; CHÉNLER, 2016; LIM; BAIRI; FONG, 2017; KRZYZANIAK, *et al*., 2019). Estas técnicas têm como principal vantagem a característica de serem multielementares e com ampla faixa linear. Além disso, elas vêm sendo amplamente

aplicadas devido aos baixos limites de quantificação, que permitem a quantificação de elementos em concentrações da ordem de $\mu g \ L^{-1}$ até $ng \ L^{-1}$. A técnica de ICP-MS tem por princípio a separação e determinação elementar a partir da diferenciação entre as razões massa/carga (m/z). A técnica de ICP-OES é baseada no monitoramento do comprimento de onda de emissão de luz, que é característico de cada elemento (TODOLÍ, *et al.*, 2002; PETTINE, *et al.*, 2007; DRESSLER, *et al.*, 2011).

Contudo, apesar das vantagens citadas, estas técnicas estão sujeitas a uma série de interferências. Alguns processos que ocorrem durante a introdução e o transporte da amostra no instrumento podem resultar em interferências espectrais e não espectrais. As principais interferências não espectrais que são observadas para estas técnicas estão relacionadas às propriedades físicas das soluções como viscosidade e densidade, uma vez que causam na taxa de nebulização, tamanho de gota e no transporte da amostra até o plasma (AGATEMOR; BEAUCHMIN, 2011). Com isso, faz-se necessário o emprego de métodos de preparo de amostras eficientes que permitam digeridos com baixos teores de carbono e com ausência de sólidos dissolvidos, uma vez que estes constituintes afetam na introdução e transporte de amostra no instrumento (AGATEMOR; BEAUCHMIN, 2011).

Interferências espectrais também são comumente observadas nessas técnicas. Na técnica de ICP-MS, a presença de carbono no plasma pode causar interferências espectrais e de matriz. O carbono dá origem a espécies moleculares interferentes, que podem ser minimizadas empregando uma cela dinâmica de reação. Além disso, os efeitos de matriz devido à presença de carbono acarretam o aumento do sinal causado pela reação de transferência de carga das espécies de C^+ para os átomos do analito. Cabe destacar que, a taxa de nebulização da amostra também pode ser alterada devido à presença de carbono, bem como pode ocorrer um deslocamento dos íons na zona analítica do plasma (PETTINE, *et al.*, 2007). Na técnica de ICP-OES, as espécies presentes na solução que são introduzidas no plasma, bem como as espécies presentes no plasma, emitem radiação. Com isso, podem ser observadas sobreposições de linhas espectrais, fazendo com que a escolha da linha espectral a ser monitorada deva ser realizada em função da ausência destas interferências, bem como do LOQ (TODOLÍ, *et al.*, 2002). Neste contexto, para determinação elementar em amostras de CNT, em ambas as técnicas, é necessário que a matriz seja eliminada para que as principais interferências sejam minimizadas. Visto que, a ineficiência na decomposição e, consequentemente, a presença de carbono no plasma pode resultar em resultados superestimados (YANG, et *al.*, 2010).

2.4   DISPOSITIVOS PORTÁTEIS EM QUÍMICA ANALÍTICA

O uso de dispositivos portáteis para obtenção de imagens digitais vem sendo aplicado cada vez com maior frequência na química analítica como técnica de determinação. Para isso, tem sido aplicado dispositivos como *scanners*, *webcams*, câmeras fotográficas digitais e telefones celulares (*smartphones*) para registro das imagens de reações colorimétricas (BENEDETTI *et al*., 2015) e entalpimétricas (BARIN, *et al*., 2015). Com a melhora dos *hardwares* e *softwares*, assim como a disponibilidade de aplicativos (principalmente gratuitos) que permitem a análise de dados de forma rápida e fácil, os *smartphones* passaram a se tornar a principal escolha para muitos pesquisadores em todo o mundo, como uma ferramenta alternativa de baixo custo para diferentes aplicações de detecção tanto biológicas, físicas e químicas, a partir da transformação das informações contidas em imagens digitais em dados analíticos (GALLEGOS, *et al*., 2013).

2.4.1 Imagens digitais

Como definição, pode-se descrever que uma imagem digital é uma matriz composta de x linhas e y colunas, constituídas por um conjunto finito de elementos de imagem (pixels). Os pixels, por sua vez são compostos por uma sequência de dígitos binários dispostos em série, comumente quadriculada, que representam uma intensidade de luz e cor, onde este conjunto de pixels integrado formará uma imagem digital. Quando adquirida, uma imagem digital terá seu tamanho caracterizado pelo número de pixels que a compõe, bem como pela resolução na qual foi adquirida, podendo o mesmo ser calculado a partir da Equação 1 (GONZALEZ; WOODS, 2010).

$$Tamanho\ da\ imagem = \frac{N°\ de\ pixels}{Resolução} \qquad\qquad \text{Equação (1)}$$

As informações de cores de uma imagem digital estão contidas em cada pixel que as compõem. Com isso, para classificar e qualificar as cores que compõem uma imagem quanto a tonalidade, saturação e luminosidade ou brilho, são empregados os modelos de cores. Em análises colorimétricas utilizando imagens digitais destacam-se a utilização dos modelos de cores RGB (do inglês *red, green, blue*), HSI (do inglês *hue, saturation,*

intensity), HSV (do inglês *hue, saturation, value*) e HSL (do inglês *hue, saturation, lightness*) (GONZALEZ; WOODS, 2010; Capitan-Vallvey, *et al.*, 2015). Neste contexto, considerando a crescente utilização dos smartphones para o desenvolvimento de técnicas de quantificação na química analítica, o uso deste dispositivo será discutido a seguir com maiores detalhes.

2.4.2 Smartphones

Os smartphones apresentam uma interface fácil de ser manipulada, dessa maneira os analistas não necessitam de treinamento para utilização do dispositivo. Por isso, o emprego dos smartphones em análises quantitativas é reconhecido como uma tecnologia inovadora e várias aplicações vem sendo desenvolvidas (HUSSAIN; AHAMAD; NATH, 2016; HUSSAIN, *et al.*, 2017).

Os smartphones abrangem uma grande faixa de resposta espectral entre 350 a 1000 nm. Devido à alta faixa dinâmica dos smartphone é possível converter a intensidade de luz, que é captada pelo sensor de luz ambiente destes equipamentos, em informação analítica. A intensidade de luz é fornecida em unidades lux (lx), onde nos smartphones a faixa é de 0 a 20.000 lx, com resolução de 0.01 lx (HUSSAIN; AHAMAD; NATH, 2017).

Os sensores baseados em intensidade luminosa são fundamentados no princípio da Lei de Lambert-Beer. Quando um feixe de luz se propaga através de um meio, a intensidade deste feixe é atenuada devido à sua absorção pelo meio. Com isso, a magnitude da absorção dependerá do comprimento de onda do feixe, da intensidade de luz incidente, do comprimento do caminho óptico e da concentração do meio. A intensidade de luz transmitida (I_T) pode ser expressa pela Equação (2):

$$I_T = I_0 e^{-\varepsilon cl}$$
Equação (2)

onde, I_0 é a intensidade de luz incidente que se propaga através do meio absorvente, l é o comprimento do caminho óptico, c a concentração da solução e ε é o coeficiente de absorção molar, que é uma função do comprimento de onda da luz incidente (HUSAIN; CHOUDHURY; NATH, 2013).

Quando o smartphone é utilizado neste tipo de análise, o comprimento de onda específico do flash do LED da câmera do smartphone é incidido sobre uma solução

colorida, gerando um sinal óptico com a intensidade luminosa da região incidida. A intensidade é detectada pelo sensor de luz ambiente do smartphone. Um aplicativo específico converte o sinal gerado em dados analíticos. Para quantificação dos íons presente em solução, as respostas do sensor para a amostra são comparadas com as das soluções padrão utilizadas na curva de calibração (HUSSAIN; AHAMAD; NATH, 2017).

Além da intensidade luminosa, as quantificações a partir do emprego de smartphones podem se basear nos valores de RGB das imagens digitais adquiridas com a câmera do smartphone ou de acessórios acoplados ao mesmo. Em análises colorimétricas utilizando imagens digitais, o modelo de cores RGB tem sido um dos mais empregados para o tratamento das imagens (BÖCK, *et al.* 2020). Estes modelos, são utilizados para classificação e qualificação das cores quanto a tonalidade, saturação e luminosidade ou brilho (COSTA, *et al.*, 2015; PENG, *et al.*, 2017).

Em análises a partir de imagens digitais, o smartphone é empregado para a aquisição das imagens da solução colorimétrica. Para isso, é necessário um ambiente com luminosidade controlada para que a mesma se mantenha sem variação, evitando interferências. Um software específico baseado na qualificação de cores pelo modelo RGB é empregado para conversão da cor em resposta analítica. Para quantificação da concentração dos íons presentes em solução, a intensidade de cor das amostras é comparada com o de soluções padrão utilizadas para a construção de curvas de calibração (PAPPIS, *et al.*, 2019).

Apesar da versatilidade e baixo custo do emprego dos smartphones e sensores para determinação elementar a partir de reações colorimétricas, cabe destacar que algumas desvantagens frente a interferentes têm sido relatadas na literatura. Interferências na determinação de Ni empregando o método colorimétrico de dimetilglioxima (DMG) pela presença de íons metálicos com Fe e Mn têm sido relatas na literatura (MOGHADDAM, 2011). Com isso, é necessária a identificação e eliminação desses interferentes frente ao emprego destes dispositivos de baixo custo para determinação elementar na química analítica.

2.4.3 Softwares para tratamento de imagens digitais

Nos últimos anos, o desenvolvimento de softwares para o processamento de imagens digitais tem aumentado significativamente. Este fato se deve ao crescente aumento da análise de imagens como ferramenta analítica. Estes softwares para

tratamento das imagens e obtenção de informações analíticas, podem ser encontrados em plataformas como o Google Play Store, alguns com acesso livre.

Um dos principais softwares de acesso livre empregados para o tratamento de imagens é o ImageJ. Para uso deste software, as imagens digitais são adquiridas por dispositivos portáteis como os smartphones e posteriormente tratadas. Este software pode exibir, editar, analisar, processar, salvar e imprimir imagens de 8, 16 e 32 bits. Além disso, o software é compatível com diversos formatos de imagem, incluindo TIFF, GIF, JPEG, BMP, DICOM, FITS e 'raw'. Para tratamento de imagens, o ImageJ pode calcular estatísticas de área e valor de pixel de seleções definidas pelo usuário. Além disso, pode medir distâncias e ângulos, criar histogramas de densidade e gráficos de perfil de linha. Este software suporta funções padrão de processamento de imagem, como manipulação de contraste, nitidez, suavização, detecção de bordas e filtragem mediana (FERREIRA; RASBAND, 2012). O software ImageJ tem sido aplicado para o tratamento de imagens como, por exemplo, para a determinação do teor de etanol em bebidas (CURBANI; GELINSKI; BORGES, 2020), determinação de cafeína em bebidas energéticas e medicamentos (LUCHIARI, *et al*., 2019), determinação de nitrito em carnes processadas (AZEEM; MADBOULY; EL-SHAHAT, 2019), determinação de ferro em alimentos e água (PENG, *et al*., 2017), determinação de Fe^{3+} em amostras ambientais e biológicas (SHRIVAS, et al., 2020a), determinação de As^{3+} em amostras de solo e água (SHRIVAS, *et al*., 2020b), exploração dos processos químicos e cinéticos envolvidos em processos fotográficos (FUDALA; JONES, 2019) e determinação de biofilmes em superfícies metálicas (VOSS, *et al*., 2020).

Além do uso de software de acesso livre como o ImageJ para tratamento de imagens, muitos pesquisadores tem desenvolvido softwares para aplicações específicas, como para o tratamento de imagens digitais para a determinação da acidez total de vinhos tinto (TÔRRES, *et al*., 2011), determinação de fluoreto em água potável (HUSSAIN; AHAMAD; NATH, 2016) e determinação de fósforo em águas naturais (COSTA, *et al*., 2016). No entanto, apesar do potencial de uso das imagens digitais, os softwares de acesso livre ou os desenvolvidos por pesquisadores para aplicações especificas, não incorporam funções para o processamento dos resultados como, por exemplo, a aplicação de técnicas de análise univariadas e multivariadas.

Neste contexto, Helfer e colaboradores (2017), desenvolveram o aplicativo PhotoMetrix. Este aplicativo é de acesso livre e foi desenvolvido para captura e análise de imagens digitais, empregando para modelos matemáticos univariados e multivariados,

como análise de componentes principais (PCA, do inglês, *Principal Component Analysis*), análise de agrupamento hierárquico (HCA, do inglês, *Hierarchical Cluster Analysis*) e regressão pelo método dos quadrados mínimos parciais (PLS, do inglês, *Partial Least Squares*). Duas versões desse aplicativo estão disponíveis para acesso gratuito no Google Play (Android) e App Store (IOS). A versão PhotoMetrix Pro permite a captura de imagens através da câmera do smartphone e a versão do PhotoMetrix UVC permite a captura de imagens a partir de uma câmera USB conectada ao smartphone (BAUMANN, *et al*., 2019). O aplicativo permite que o usuário defina o número de amostras, identifique-as, e escolha o tamanho da região de interesse para a amostragem (ROI), podendo ser regiões de 32×32, 48×48, 64×64 ou 96×96 pixels. Além disso, permite a utilização do flash no momento da aquisição das imagens e envio dos dados diretamente para o endereço de e-mail cadastrado no aplicativo (HELFER, *et al*., 2017). O aplicativo PhotoMetrix tem sido utilizado para a determinação de flúor em água (BAUMANN, *et al*., 2019), determinação de fósforo e flúor em águas de consumo (PAPPIS, *et al*., 2019), determinação de ferro em suplementos vitamínicos (HELFER, *et al*., 2017), determinação de etanol em aguardente de cana-de-açúcar (BÖCK, *et al*., 2018) e análise de extratos comerciais de tanino (GRASEL, *et al*., 2016).

3 DISCUSSÃO

Nesta seção estão descritos, na forma de manuscritos, os resultados obtidos com os experimentos realizados, com destaque principal para a MIC-DV como método de preparo de amostras e diferentes tipos de sistemas de detecção para Ni e La em CNT. O primeiro manuscrito consiste no emprego da MIC-DV decomposição de amostras de CNT para posterior determinação de Ni por técnicas espectrométricas. Para isso, foram realizadas otimizações da MIC-DV para obtenção das melhores condições de operação do sistema, sendo avaliadas a massa de amostra, pressurização e purga do frasco e volume e concentração da solução absorvedora. Como método comparativo de preparo de amostra foi utilizada a MAD-SRC. Para determinação de Ni foi utilizada a técnica de ICP-OES, posteriormente foram otimizadas as condições do sistema de determinação colorimétrica proposto. Os resultados da concentração de Ni obtidos nos digeridos empregando as técnicas espectrométricas convencional e a proposta no presente estudo, foram avaliados estatisticamente.

No segundo manuscrito são mostrados os resultados referentes a determinação La em CNT após preparo da amostra empregando MIC-DV. Neste estudo, foi empregado MIC-DV com sistema pressurizado e como método comparativo de preparo de amostra foi utilizada a MIC. Para obtenção das melhores condições do sistema MIC-DV foram avaliados volume e concentração da solução absorvedora e pressão do sistema. A concentração de La em ambos os digeridos foi determinada empregando a técnica espectrométrica de ICP-OES e os resultados comparados e avaliados estatisticamente.

Além disso, foi realizada a avaliação do desempenho dos métodos propostos frente aos princípios da química analítica verde. Para isso, foi utilizada a ferramenta WAC (White Analytical Chemistry), onde foram considerados aspectos como a performance analítica dos métodos, impactos ambientais gerados e a praticidade e custo envolvido na utilização destes métodos.

Manuscrito 1: **MIC-DV combined with smartphone-based colorimetric detection for Ni determination in carbon nanotubes**

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MIC-DV combined with smartphone-based colorimetric detection for Ni determination in carbon nanotubes

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Abstract

This work presents the really first application of microwave-induced combustion in disposable vessels (MIC-DV) for Ni determination in carbon nanotubes (CNT) using a smartphone-based colorimetric (SBC) detection system. Considering the difficulties concerning the CNT digestion, a careful optimization of MIC-DV was performed, evaluating the sample mass, type and volume of absorbing solution, way of filling the vessel with oxygen. The colorimetric determination was based in the reaction between dimethylglyoxime (DMG) and Ni in the presence of an oxidant reagent. The iodine was used as an oxidant reagent and tartaric acid was used to eliminate de iron interference with the complexation of nickel. A free PhotoMetrix UVC software was used for operating a USB video camera (UVC) and for multivariate image analysis. An UVC was positioned in an open-source 3D printed chamber illuminated by a white light-emitting diode (LED) with controlled intensity of light. The influence of illumination intensity and concentration of complexing reagent were evaluated to achieve the best condition of colorimetric determination. The parameters chosen in the MIC-DV method were 5 mg of CNT, 5 mL of HNO_3:HCl (1:1) as absorbing solution and pressurization up to 1 bar of O_2. For the colorimetric determination, 0.1% dimethylglyoxime (DMG) and 15 lux of illumination intensity were used. The performance of MIC-DV was compared with MAD using colorimetric determination by smartphone-based method (SBC). The colorimetric determination also was compared with ICP-OES in the digests from MIC-DV and MAD. The proposed MIC-DV/SBC method presented good agreement with the conventional methods, ranging from 96 to 104%. The analytical performance and system cheapness are important characteristics that increase the use of CNT for further Ni determination in several laboratories.

1. INTRODUCTION

Currently, one of the most challenging in green analytical chemistry (GAC) is the development of sample preparation methods with low environmental impact.[1] The most of sample preparation methods present several steps, making the process time consuming and susceptible to errors, affecting the precision and accuracy of the results.[2] In addition, according to the high chemical resistance of some matrices (e.g., carbon nanotubes, CNT), the use of high reagents amount during the sample preparation is required.[3]

Carbon nanotubes are an allotropic form of carbon, characterized by a tubular structure. This nanomaterial can be classified as single-wall carbon nanotube (SWCNT) or as multi-wall carbon nanotube (MWCNT).[4] Carbon nanotubes (CNT) have been applied for the development of materials for industrial applications,[5] electronic equipment,[6] medicines,[7,8] biotechnology,[8] among others.[4] During the CNT synthesis, some metallic catalysts are generally used (e.g., Ni, Fe, La and Co), requiring a further purification step. However, many elements, such as Ni, can be present in the material in relatively high concentration, affecting the physical, chemical, and surface properties of CNT.[9] Therefore, the impurities can be highly toxic if inhaled by living organisms, making necessary the development of methods for quality control of inorganic contaminants in CNT.[10]

Microwave-assisted digestion (MAD) in closed vessels have been considered as the state-of-the-art among sample preparation method for further elements determination by spectrometric techniques.[11] Although MAD have been described as an efficient, fast

and safe method, some limitations regarding to sample mass, greater amounts of reagents and longer digestion time have been highlighted.[3,12]

Microwave-induced combustion (MIC) was proposed as an alternative to overcome the main limitations of MAD, mainly for the digestion of organic matrices.[13,14] MIC combines the advantages of MAD with those of combustion methods in closed systems, allowing the use of diluted solutions, reducing the reagents amount, as well the risks of contamination.[15,16] It is important to mention that the conventional sample preparation methods (MAD and MIC are included) require the digests transferring to volumetric flasks and filling up to the desirable volume, diluting the digest and compromising the limits of quantification.

These limitations makes MIC in disagreement with some of the GAC principles, which are the integration and miniaturization of processes.[17] In addition, the commercial MIC system present a relatively high acquisition cost. In this context, the microwave-induced combustion in disposable vessels (MIC-DV) was recently proposed as an alternative.[18-21] MIC-DV consists of using a domestic microwave oven and polypropylene disposable vessels, where only the quartz holder must reused.[18,19] This method allows the reduction of reagents volume (e.g., typically, below 5 mL), as well as the sample preparation and analytes quantification are performed in the same vessel, according to the single-vessel principle by using the disposable vessels,[18,19] which is practically in full agreement with GAC principles.

Although the conventional spectrometric techniques remain as the most common approaches for elements determination, in recent years, the development of detection techniques (combined with sample preparation methods) have allowed to perform chemical analyzes with high precision, accuracy and low cost.[22] In this context, the use of devices such as smartphones has been proposed as an emerging technique, allowing of

field analyzes with quick results, due to the portability.[23-27] As a result of such developments, digital image analysis (DIA) techniques or digital image-based (DIB) methods have been used for quantitative analysis, mainly due to its low cost.[24,25,27,28] In this strategy, devices for capturing digital images, such as cameras, webcams, scanners and smartphones with a built-in camera (charge-attached devices) have been used for recording images of colorimetric[29] and enthalpimetric[30-32] reactions, where the variation in the color intensity or enthalpy of a reaction are identified, respectively.

Considering the development of sustainable, low-cost, and portable analytical instruments, the present work proposes the use of MIC-DV as a sample preparation method, combined with the use of smartphones for further determination of Ni in CNT. A polymeric (polypropylene, PP) disposable vessel was used for sample combustion. The colorimetric determination was performed using an endoscopic camera adapted to a 3D-printed device connected to the smartphone via USB. The analytical parameters were optimized, such as volume and concentration of a complexing solution (for the colorimetric reaction), the proportion of solutions, time, pH and illumination. For the treatment of digital images, the free android app PhotoMetrix UVC was used, and the results were compared with analytes determination by inductively coupled plasma optical emission spectrometry (ICP-OES) after CNT digestion by MAD.

2. EXPERIMENTAL

2.1 Instrumentation

The MIC-DV system consists of a domestic microwave oven (BMK38LQBNA, Brastemp, Brazil), with a lab-made metallic rotor for supporting the commercially available disposable PP vessels (Sarstedt, 50 mL, Germany). Quartz holders were specially developed for sample introduction into the PP vessels. For purging or

pressurizing the vessels with oxygen a capillary tube (3.5 mm O.D., 2.5 mm I.D., 150 mm of length, made of perfluoroalkoxy alkane) was connected to a flowmeter (FR 2000 series, Key Instruments, USA). For the purged system, the capillary tube was inserted into the vessel (Figure 1A). For the pressurized system, an adaptation of the PP cover vessels was performed (Figure 1B).
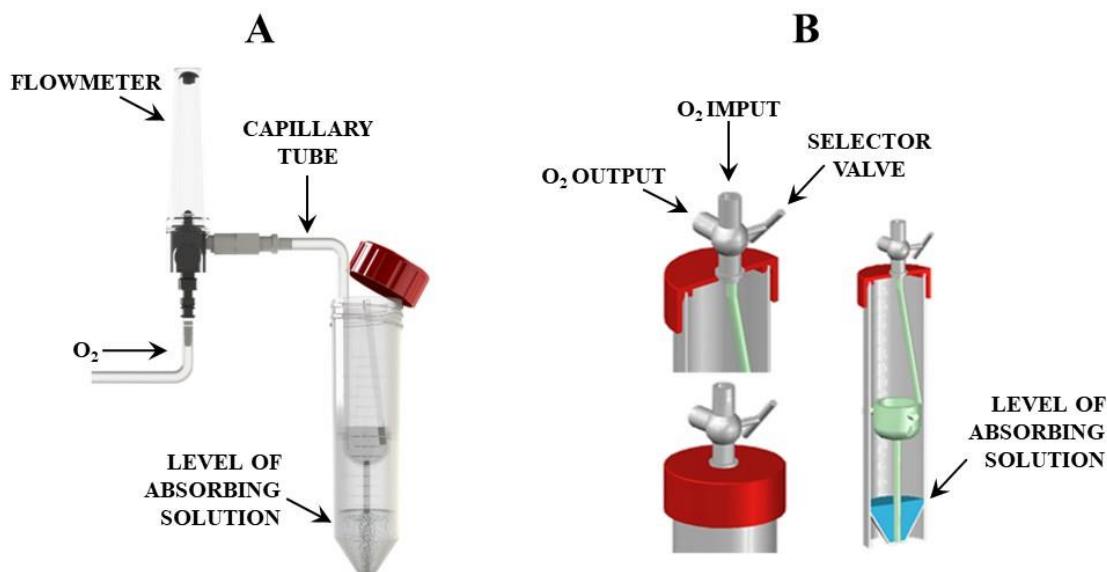
Figure 1. Proposed MIC-DV for sample preparation system using purged and pressurized method. A) Vessel purging apparatus (flowmeter and capillary tube). B) Vessels pressuring apparatus (selector valve and hole to output and input O_2).

For Ni colorimetric determination, digital images were obtained using an endoscopic camera (model Intelligent Endoscope, SmartCam, 7 mm and resolution of 640 x 480 pixels) connected to a smartphone (model Galaxy J5 Pro, Samsung, USA). A chamber containing a white LED lamp (with illumination intensity control) was manufactured in a 3D printer (model Core A3, GTMAX3D, Brazil), as shown in Figure 2. The chamber contains two compartments for inserting the PP tube (Sarstedt type, 15 and 50 mL, Germany). A hole in the side of both compartments was used for inserting the endoscopic camera. The images with the region of interest (ROI) of 64 x 64 pixels

were captured after the colorimetric reaction and processed using a smartphone equipped with a free software PhotoMetrix UVC (version 1.0.7, GHELFER.NET Inc.), available at Google Play store. The multivariate calibration mode by PLS regression was selected in the software using RGB histogram values.

Figure 2. Proposed device for colorimetric determination of Ni. (A) smartphone for PhotoMetrix UVC software operation. (B) Endoscopic camera connected via USB for obtaining the digital images. (C) Chamber for PP vessel supporting and reactional luminosity control.
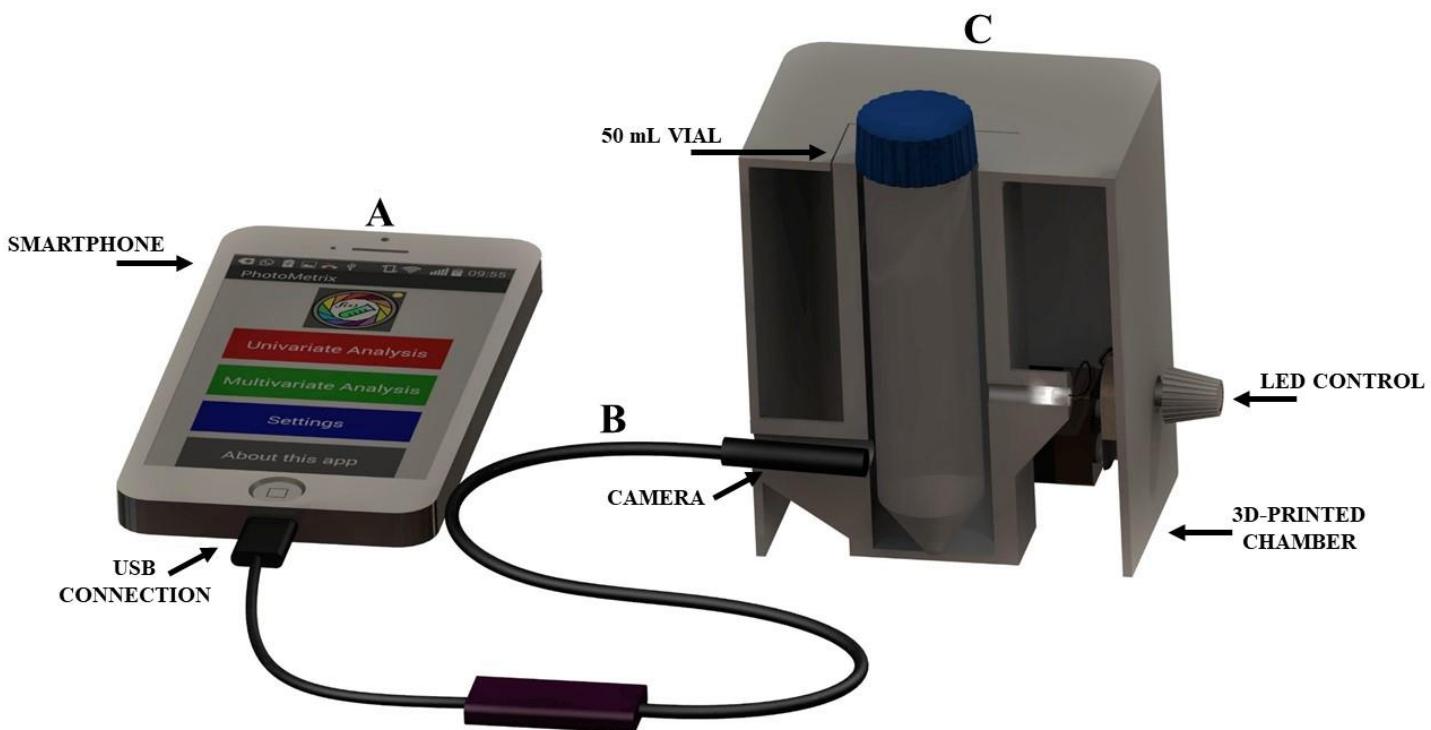
For results comparison, MAD with single reaction chamber (MAD-SRC) was used employing a microwave sample preparation system (Ultrawave™, Milestone, Italy). This system allows the use of 15 quartz vessel (total volume of 15 mL each vessel) and an 1 L microwave cavity (stainless steel with a polytetrafluoroethylene cover). Although the system allows the application of 300 °C and 199 bar, the temperature and pressure were set at 270 °C and 160 bar, respectively. Before microwave irradiation program,

chamber was sealed and pressurized with 40 bar of argon (99.996%, White Martins, Brazil) and vessels were irradiated with a maximum power of 1500 W.

After digestion by MAD-SRC, Ni determination was performed using an inductively coupled plasma optical emission spectrometer with axial view configuration (model Spectro Ciros CCD, Spectro Analytical Instruments, Germany). The operational conditions were radiofrequency power of 1400 W; argon flow rate for plasma, auxiliary and nebulizer gases were set at 12, 1.0, and 1.00 L min^{-1}, respectively. Emission lines were set at 231.604, 193.091 and 371.030 nm for Ni, C and Y, respectively.

2.2 Samples, standards and reagents

Two commercial MWCNT samples (named CNT-1 and CNT-2) were used in this work. CNT-1 is functionalized with COOH groups and present 95% of minimum purity and 1.47-1.63% mass fraction. CNT-2 is functionalized with OH groups and present 95% of minimum purity and 2.36-2.60% mass fraction.[33] Samples were dried at 105 °C in an oven for 120 min (Nova Ética, Brazil). For all optimizations was used the sample CNT-1. A certified reference material (CRM) of SWCNT (2LV-BIO-SWCNT-1), provided by National Research Council Canada, was also used.

Ultrapure water was obtained in a Milli-Q system (Direct-Q 3 UV, 18.2 MΩ cm, Millipore Corp., USA). HNO$_3$ (65%, 1.4 kg L^{-1}, Merck, Germany) and HCl (37%, 1.19 kg L^{-1}, Merck) were distilled in a sub-boiling distillation system (model duoPUR, Milestone, Italy). Both acids were evaluated as absorbing solutions for MIC-DV. Ammonium nitrate (Merck) was used as igniter, prepared by dissolving the salt in ultrapure water. This solution was used by adding it in low ash filter paper discs (Black Ribbon Ashless, Schleicher & Schüll GmbH, Germany) which are used as aid of combustion process. The pellets of ammonium chloride (Merck, Germany) were used as

an additive to avoid the oxides formation. The filter paper discs were cleaned as previously described in the literature.[18] Oxygen (99.6%, White Martins-Praxair, Brazil) was used for purging or pressurization of MIC-DV system.

For the colorimetric Ni determination, solutions of dimethylglyoxime (DMG) with concentration ranging from 0.10 to 0.30 mol L^{-1} were evaluated. The DMG solutions were prepared in 50% (w/v) NH_4OH solution. For complexation reaction, a 0.1 mol L^{-1} iodine solution was used. The pH adjustment for the complexation reaction was performed by 20% (w/v) tartaric acid solution.

For the determination of dissolved carbon in digests, a stock reference solution of 1000 mg L^{-1} C was used and prepared by dilution of citric acid (Merck, Germany) in water. The C reference solutions with concentration from 5 to 500 mg L^{-1} were prepared by sequential dilution of the stock reference solution. Yttrium (1000 mg L^{-1}, Spex, USA) was added as internal standard in samples, standards, and blanks at final concentration of 1 mg L^{-1}. For the measurements by ICP-OES, the reference solutions were prepared by dilution from a 10 mg L^{-1} multielement stock solution (SCP33MS, SCP Science, Canada) in 0.7 mol L^{-1} HNO_3, with concentration ranging from 2.5 to 500 µg L^{-1}. Argon (99.996%, White Martins) was used for the measurements by ICP-OES.

2.3 Microwave-assisted digestion

The MAD method was designed from a work proposed by Krzyzaniak and collaborators.[3] About 25 mg of CNT were directly weight into the quartz vessels and digested using 6 mL of 14.4 mol L^{-1} HNO_3 + 0.5 mL of 30% H_2O_2. The rack containing the previously prepared quartz tubes was inserted into the SRC chamber. The SRC chamber was filled with 120 mL of water and 5 mL of concentrated HNO_3 and after this, the system was pressurized with argon up to 40 bar before the microwave irradiation. The

microwave irradiation program was: *i)* ramp of 10 min up to 180 °C and hold for 15 min, *ii)* ramp of 5 min up to 270 °C and hold for 35 min and *iii)* 40 min of cooling. The digests were transferred to PP vessels (identical to those used in MIC-DV method as described below), diluted with ultrapure water and analytes further determined by ICP-OES.

2.4 Microwave-induced combustion in disposable vessels

Pellets (5 to 20 mg) of samples were prepared using a hydraulic press (Specac, Orpington, UK) set at 1 ton. The filter paper was placed in the quartz holder and 40 µL of 10 mol L^{-1} NH_4NO_3 solution were added. After weighing, the sample was placed over the filter paper on the quartz holder. Five milliliters of absorption solution were transferred to the PP vessels and the quartz holder containing the sample was inserted into the PP vessel. For purging, a capillary tube was insert into the vessel (without contact with the solution) and purging with oxygen was started. After that, the vessels were closed, inserted in the metallic rotor, which was positioned into the microwave oven cavity and vessels were irradiated (at maximum power) for about 30 s or up to start the combustion in all the vessels. Immediately after stopping the irradiation, the vessels were removed from the metallic rotor and manually shaken for analytes absorption. After 1 min shaking, the vessels were opened, and the quartz holders were removed. It is important to highlight that the pressurization of the MIC-DV system also was evaluated. Thus, the cover of PP vessels was adapted for pressurization with oxygen. The cleaning of quartz holder was performed by immersion in a glass beaker containing 7 mol L^{-1} HNO_3 solution, which was maintained under boiling for 30 min in a hotplate.

The optimization of the MIC-DV method was performed using the sample CNT-1. Initially, a qualitative experiment was performed for the evaluation of sample mass that could be burned in the MIC-DV using purged and pressurized systems. Sample pellets

containing 5, 10, 15 and 20 mg were burned in both systems. For all the evaluations, the purging with oxygen was set at 4 L min^{-1} for 10 s (time selected after optimization; results not shown) and the pressurization was carried out reaching 1.0 bar of oxygen. The sample mass that could be burned in the MIC-DV system was evaluated as a function of the solids remaining in the quartz holder after combustion and in both systems, as well as a possible overpressure. To improve an analyte recovery, NH_4Cl pellets was added as an additive to avoid the oxides formation. Thus, NH_4Cl pellets was added to the sample pellets for combustion, the proportion of sample pellets mass and NH_4Cl pellets were 1:1. Afterwards, 5 mL of H_2O, HNO_3 (6, 8, 10, 12 and 14 mol L^{-1}) and the mixtures of concentrated HNO_3 and HCl 3:1 (3.75 mL and 1.25 mL, respectively), 2:1 (3.33 mL and 1.67 mL, respectively) and 1:1 (2.5 mL and 2.5 mL, respectively) were evaluated as absorbing solutions for MIC-DV. The influence of the volume of absorbing solution was also evaluated 5, 7.5 and 10 mL). The limit of detection (LOD, 3σ) and limit of quantification (LOQ, 10σ) were calculated considering the average of the blanks according to the Eurachem Guide.[34]

2.5 Optimization of colorimetric smartphone-based determination

For the colorimetric determination of Ni, the concentration of complexing solution (DMG 0.1 mol L^{-1}) and light intensity of the LED lamp (2 to 75 lux) were evaluated. The control of light intensity of LED lamp was measured in five values using a free software (CPU-Z for Android, version 1.29, 2019), available at Google Play.

The calibration curve prepared with Ni concentration ranging from 0.25 to 2.0 mg L^{-1}. Starch stock solution (10 mg L^{-1}) was prepared previously SBC calibration. Afterwards, for the preparation of calibration curve, an aliquot of Ni solution was added and 5% HNO_3 solution was added to reach 1 mL, followed by adding of 1 mL of 0.1 mol

L^{-1} iodine solution, 1 mL of 20% (w/v) tartaric acid and 2 mL of DMG. The same condition was used to Ni determination in the digests of the samples. The vessels containing the complex Ni-DMG were inserted in the detection chamber and the images were obtained under controlled illumination (without interference of ambient light). Images with 64×64 pixels in the ROI were captured after the colorimetric reaction and processed in the smartphone by the PhotoMetrix UVC app. The PLS model was selected in the software using RGB histogram values.

2.6 Statistical evaluation

The data were evaluated using analysis of variance (ANOVA, one-way) followed by student's t-test with 5% of significance level, using Statistica 5.1 (Statsoft, 2004, USA) software. PLS regression results were evaluated according to the coefficients of determination (R^2), slope, offset, root mean squared error of calibration (RMSEC), root mean squared error of cross-validation (RMSECV) and root mean squared error of prediction (RMSEP), also using the same software.

3. RESULTS AND DISCUSSION

3.1 Evaluation of MIC-DV system

Initially, CNT-1 was digested by the procedure of microwave-assisted digestion (MAD) proposed in the literature[3] and Ni was determined by ICP-OES. The Ni concentration found in CNT-1 (15703 ± 791 µg g^{-1}) was considered as the reference value for the optimization of MIC-DV. The evaluation of the sample mass was the first parameter that was evaluated, but the initial experiments were performed qualitatively only observing if the sample was burned. Therefore, purged and pressurized systems were used applying sample mass of 5, 10, 15, and 20 mg. The experiments were performed

using 40 μL of NH_4NO_3 10 mol L^{-1} and purging for 10 s (4 L min^{-1} O_2) or O_2 pressurization up to 1 bar. The results are shown in Figure 3.
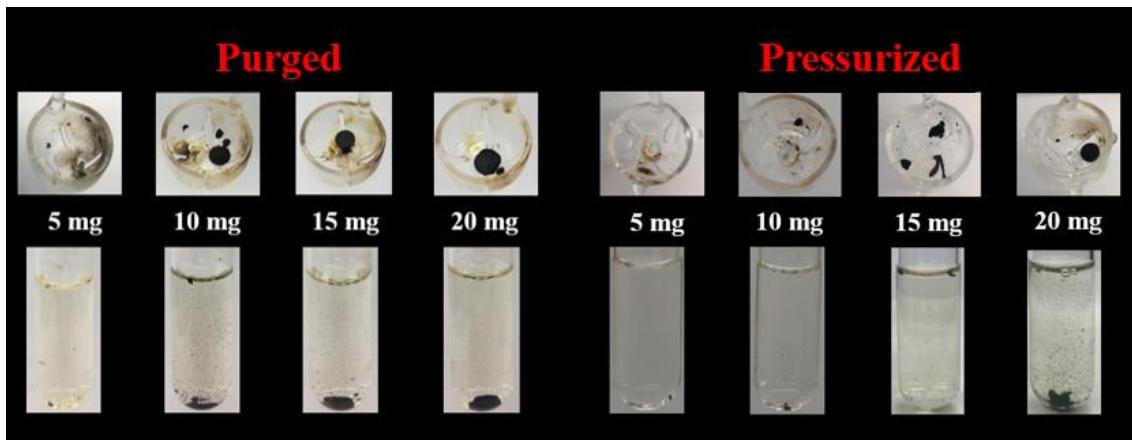
Figure 3. MIC-DV applying different samples masses in the purged and pressurized systems. The squares (upper part) are the base of quartz holder and rectangles (down part) are the aspect of the digests transferred to a glass tube.

Considering that the O_2 amount inside the vessel of MIC-DV is limited, when comparing the sample mass that could be digested by MAD, the sample amount digested by MIC-DV system is very low. However, there are some positive aspects that justify the use of MIC-DV, such as the similar sample mass/volume of absorbing solution ratio, being about 4 mg/mL for MIC-DV and 10 mg/mL for MAD.[18] It is important to point out that MIC-DV operates at the limit of oxygen amount in the system and the study about the maximum sample mass present a great relevance.

It was possible to observe (Figure 3) that in the purged system, no more than 5 mg were burned completely and presented a clear absorbing solution. For higher sample masses evaluated, the burning was incomplete and the sample pellets (or part of them) remained on the quartz holder after "burning". However, in the pressurized system, the burning was complete for 5 and 10 mg of CNT. After that, the quantitative evaluations

were started using 5 mg of CNT-1 in purged and pressurized systems using 5 mL of HNO_3 6 mol L^{-1} as absorbing solution, 40 μL of NH_4NO_3 10 mol L^{-1} and purging for 60 s (4 L min^{-1} O_2) or pressurization with 1 bar of O_2. Applying these conditions, the recoveries (data not shown) in the purged and pressurized systems were only 5 and 29%, respectively. It is important to mention that some elements as Ni can form oxides in the quartz holder surface, preventing it from being transferred to the absorbing solution.[15] Thus, some additives like NH_4Cl can be used to avoid the oxides formation, improving the analyte volatilization from the matrix.[35]

Thus, the use of NH_4Cl was evaluated (1:1, sample: additive mass ratio) in both purged and pressurized systems. The NH_4Cl pellet was prepared separately and using the same conditions of the CNT pellets. The NH_4Cl pellets was added on top of each other just before the combustion using MIC-DV. After using NH_4Cl, the agreement with reference values (data not shown) was increased to 16 and 38% for purged and pressurized systems, respectively, which was not enough for quantitative purposes.

Considering the increasing in Ni recovery using NH_4Cl pellets together with the CNT pellet and that recoveries greater than 30% were possible just in the pressurized system, the next experiments were carried out only using the pressurized system. The absorbing solution volume was also evaluated, to understand whether the low Ni absorption was related to low volatility or to the volume of absorbing solution available inside the vessel. Thus, volumes of 5, 7.5 and 10 mL of 8 mol L^{-1} HNO_3 solution were tested, and the results are shown in the Figure 4.
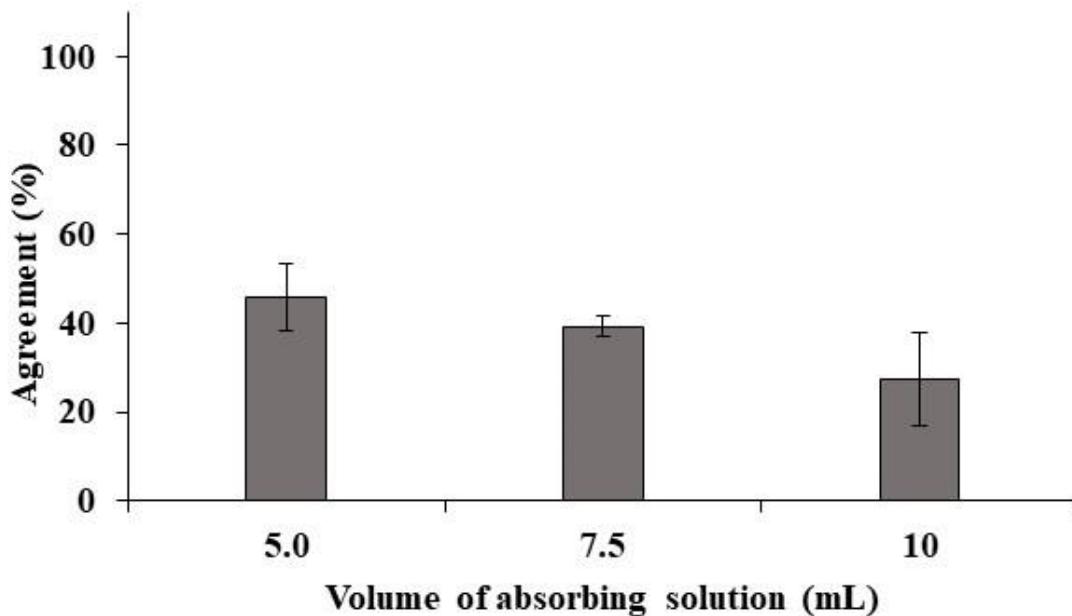
Figure 4. Effect of the volume of 8 mol L^{-1} HNO$_3$ as absorbing solution in MIC-DV for Ni determination in CNT-1. The measurements were performed using 5 mg of CNT-1, 5 mg of NH$_4$Cl, 40 μL of NH$_4$NO$_3$ 10 mol L^{-1} and pressurization up to 1 bar of O$_2$. The bars represent the agreement (%) with the reference values (MAD-SRC/ICP-OES) and the error bars represent the standard deviation (n = 5).

According to the literature[36] concentrated HNO$_3$ has been widely used for the digestion of organic matrices, considering its high oxidation power and availability at high purity. In addition, the efficiency of HNO$_3$ can be improved when mixed with of HCl (forming NOCl), which present a high oxidation power.[37] Therefore, the next experiments were performed using water, HNO$_3$ (6, 8, 10, 12 and 14 mol L^{-1}) and the mixtures of both concentrated HNO$_3$ and HCl as 3:1 (3.75 mL and 1.25 mL, respectively), 2:1 (3.33 mL and 1.67 mL, respectively) and 1:1 (2.5 mL and 2.5 mL, respectively) as absorption solution. Pellets of NH$_4$Cl continued to be used, in the same proportion (1:1).[35] The results are shown in Figure 5.
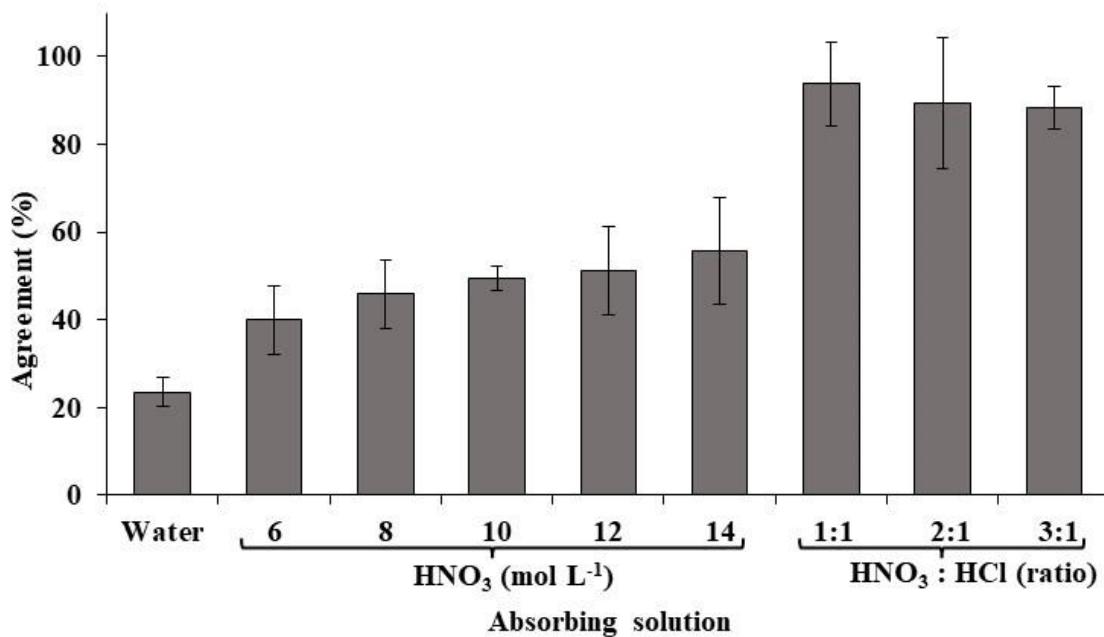
Figure 5. Influence of absorbing solution for Ni recovery in CNT-1 using MIC-DV. The measurements were performed using 5 mg of CNT-1, 5 mg of NH_4Cl, 5 mL of absorbing solution, 40 μL of NH_4NO_3 10 mol L^{-1} and pressurization up to 1 bar of O_2. The bars represent the agreement (%) with the reference values (MAD-SRC/ICP-OES) and the error bars represent the standard deviation (n = 5).

As can be seen in Figure 5, using the mixture of HNO_3 and HCl (1:1), the Ni recovery reached 94%. In addition, use these conditions, no statistical difference (Student's t-test, $p > 0.05$) was observed between the results obtained from the proposed method (MIC-DV) and reference values. Although the 3:1 condition also presented a lower RSD value, the agreement for the values obtained with the 1:1 condition was better. Thus, 5 mL of HNO_3 and HCl 1:1 was used as absorbing solution in subsequent experiments. It is important to emphasize that the effect of pressurization of MIC-DV system (up to 1.8 bar) was also evaluated (Figure S-1, see supplementary material), but no statistical difference (Student's t-test, $p > 0.05$) was observed on Ni recovery. It should be mentioned that

optimizations were not carried out with pressures greater than 1.8 bar due to damage caused to the vessel wall.

Regardless of whether it presented no difference, the oxygen amount inside the vessel should be considered. The calculation of the maximum theoretical sample mass that can be burned[38] in the MIC-DV allows to estimate: *i)* volume of O_2 available inside de vessel; *ii)* sample composition; *iii)* volume of absorbing solution; *iv)* quartz holder size and *v)* sample mass paper disc. For MIC-DV, this calculation was performed in the first publication[18] for a certified reference material (CRM, NIST 1570, spinach leaves). For CNT, this calculation was adapted and the O_2 amount in combustion vessel was considered as 2.0 mmol of O_2 and results are shown in Table 1.

Table 1. Relation between sample mass and oxygen amount for stoichiometric combustion reaction in MIC-DV system.

Sample* mass (mg)	O_2 need (mmol)	O_2 excess (%)
5	0.9	132
10	1.3	59
15	1.7	20
20	2.1	-3

* CNT-1

In theory, for a stoichiometric combustion, up to 19 mg of sample could be burnet.[38] As can be seen in table 2, when 5 mg of sample is burned using 1 bar of O_2, there is an excess of O_2 inside the combustion vessel. Therefore, no statistical difference (Student's t-test, $p > 0.05$) was observed on results when the system was pressurized with more than 1 bar of O_2 (Figure S-1, see supplementary material).

After the selection of the most suitable operational conditions for MIC-DV (5 mg of sample mass; 5 mg of NH_4Cl as additive; 5 mL of HNO_3 and HCl mixtures (1:1) as absorbing solution and pressurization system with 1 bar of O_2), the dissolved carbon was determined by ICP-OES and the concentration less than 270 mg L^{-1}. It is important to highlight that carbon concentration below 5000 mg L^{-1} do not cause interferences metals determination using plasma-based techniques.[39] Thus, two CNT samples (CNT-1 and CNT-2) and one CRM were digested by MIC-DV for subsequent Ni determination by ICP-OES and results are shown in Table 2.

Table 2. Results Ni determination by ICP-OES in CNT samples and CRM after digestion by MAD-SRC and MIC-DV (results represent the mean $\pm$ standard deviation in $\mu g\ g^{-1}$, n = 3).

Sample	MAD-SRC	MIC-DV
CNT-1	15703 $\pm$ 791	16012 $\pm$ 1431
CNT-2	20424 $\pm$ 1134	19210 $\pm$ 1228
CRM 2LV-BIO-SWCNT-1[*]	-	12975 $\pm$ 1227

[*]Certified value: 14400 $\pm$ 800 $\mu g\ g^{-1}$

For samples CNT-1, CNT-2 and CRM, the agreement with reference or certified values ranged from 90 to 102%, respectively, which were considered excellent considering the simplicity of MIC-DV and the complexity of the samples. The precision of MIC-DV method, expressed in terms of relative standard deviation, ranged from 6 to 9%.

The LOD (3σ) and LOQ (10σ) achieved for the proposed method was 35 and 115 $\mu g\ g^{-1}$, respectively. The LOQ value can be considered relatively low and with LOQs that

are considered suitable for the analyte determination in the concentration levels present in the samples used in this work.

Until here, there is a suitable number of results for a new, fast, low-cost, and simple analytical method for Ni determination in CNT. However, for improving the portability-related aspects of the method, a smartphone-based colorimetric (SBC) Ni determination was proposed, as described below.

3.2 Smartphone-based determination

3.2.1 Evaluation of operational parameters

Nickel is usually present in the +2 oxidation state, forming a 1:1 stoichiometric complex with DMG. However, this complexation process is pH dependent.[40] According to the literature,[41,42] The most suitable pH for complex (Ni + DMG) formation is between 9 to 11. Therefore, the pH of digests from MIC-DV was adjusted to ensure the best conditions for complexing and Ni detection by the SBC method. The regression models were developed using 9 calibration samples. The illumination conditions are also considered a critical parameter in colorimetric determination using SBC methods.[43] Thus, the lighting (lux) was evaluated to identify the suitable conditions for image acquisition. For these experiments, five light intensities as 2, 5, 15, 35 and 75 lux were evaluated. The results are shown in Table 4.

To obtain an adjusted PLS model, it is important that the values of the calibration errors (RMSEC) and root mean squared error of cross-validation (RMSECV) are small. Consequently, when there is an adjusted PLS model, the sample prediction error values (RMSEP) are also small. Therefore, it is possible to observe in Table 4, that were used 2 and 75 lux, the highest RMSEC and RMSECV values were obtained furthermore, it was necessary to use a greater number of latent variables (LVs) to adjust the calibration model.

As described in the literature,[27] when applied higher luminosity it is possible to achieve the highest RGB values. However, was observed during the experiments of this work that applying a high intensity of illumination a greater variation of the results was obtained. Therefore, when was used the lighting at 15 lux, the lowest RMSEC and RMSECV values were obtained, 0.03410 and 0.39565, respectively. Therefore, the 15 lux luminosity condition was chosen to follow the other optimizations. The results are shown in Table 3.

Table 3. PLS results of light intensities for Ni determination in CNT using SBC method. The measurements were performed using 0.2% (w/v) DMG, 20% (w/v) tartaric acid and 0.1 mol L^{-1} iodine solutions.

Lighting (lux)	Sample	LVs	Slope	R^2_{Cal}	RMSEC/ (mg L^{-1})	RMSECV/ (mg L^{-1})
2	9	4	0.9990	0.9987	0.04175	0.79561
5	9	3	0.9996	0.9995	0.02771	0.57714
15	9	3	0.9988	0.9992	0.03410	0.39565
35	9	4	0.9990	0.9991	0.03548	0.65163
75	9	7	0.9988	0.9989	0.04134	0.75875

The complexation conditions were also evaluated and DMG concentration was varied as 0.1. 0.2 and 0.3% (w/v) are shown in Figure 6. The addition of tartaric acid in the colorimetric reaction was carried out to eliminate the interference of iron, aluminum and chromium ions that could be present in the sample. Iodine was used as an oxidizing agent in the reaction. Both the tartaric acid solution and the iodine solution were added in excess, and it was not necessary to optimize the concentration and volume of these reagents. The PLS regression model was developed using 9 samples for calibration. The best results for calibration (RMSEC) and cross validation (RMSECV) errors were obtained with 3 LVs (factors). The determination coefficient (R^2Cal) for the proposed method was higher than 0.99 and no significant difference ($p < 0.05$) between the

predicted and measured values were identified. Thus, the DMG concentration of 0.1% was used for Ni determination using the proposed SBC method.
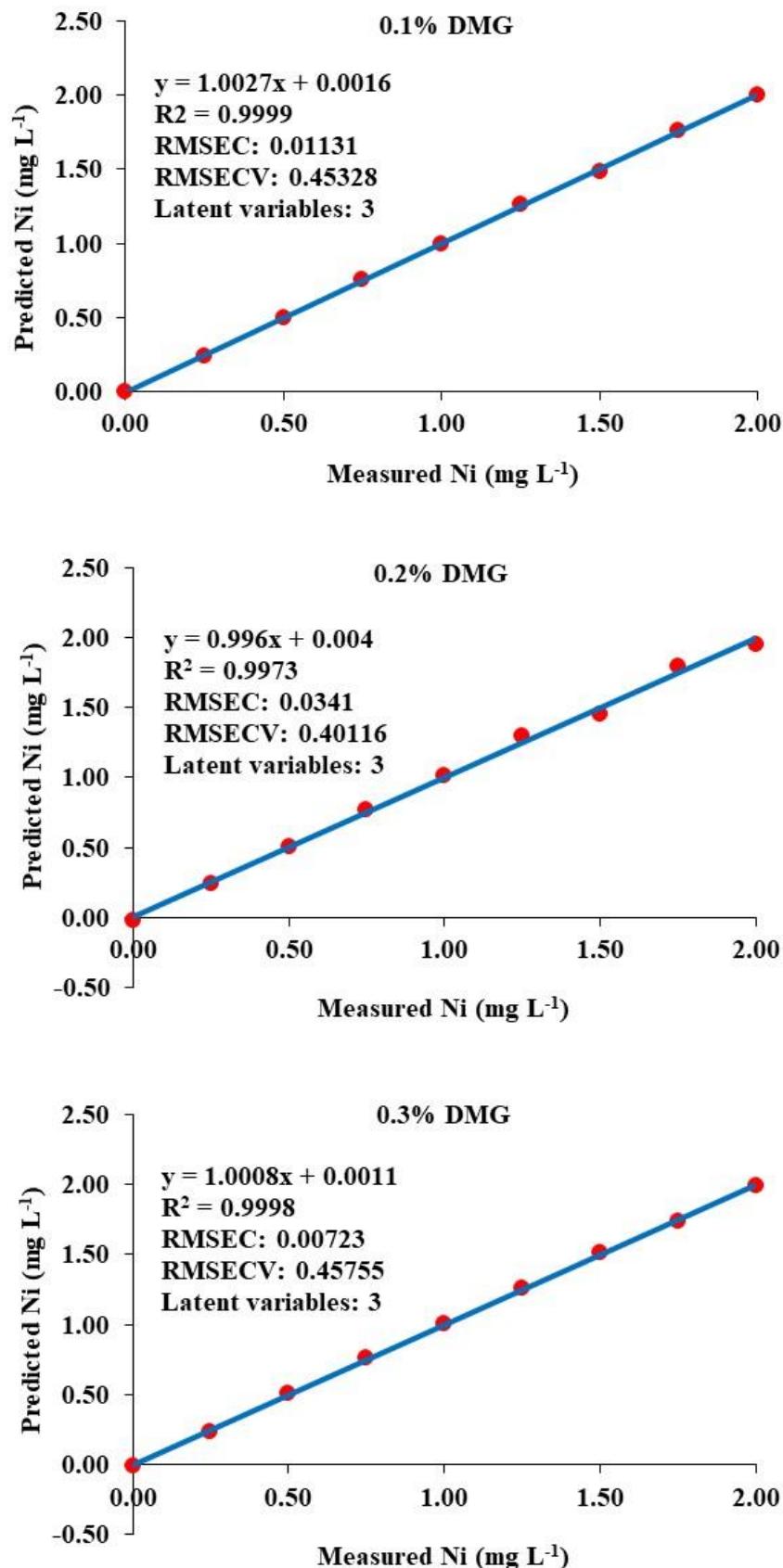
Figure 6. Effect of DMG concentration in the correlation between the predicted and measured values for Ni determination by SBC method.

3.2.2 Colorimetric Ni determination in CNT

After the optimization of the experimental conditions for the colorimetric determination by smartphone-based method, the calibration model was saved in the app and the samples were evaluated (n = 9 for each one). Thus, 200 µL of sample aliquot were added in the vessels and 5% HNO_3 solution was used to complete 1000 µL, followed by adding of 1000 µL of iodine 0.1 mol L^{-1}, 1000 µL of tartaric acid 20% (w/v) and 2000 µL of DMG 0.1% (w/v). The results are shown in Table 4.

PLS model provide prediction errors (RMSEP) less than 0.078 and 0.044 mg L^{-1} for MIC-DV and MAD, respectively. For the CNT-1 and CNT-2, agreements by using SBC ranged from 96 to 104% and from 96 to 97%, respectively, when compared to the those obtained by ICP-OES determination. It is important to mention that the LOD and LOQ values for MIC-DV/SBC were 0.05 and 0.08 mg L^{-1}, respectively.

Table 4. Results for Ni determination by SBC in CNT samples and CRM after digestion by MAD-SRC and MIC-DV. Results represent the mean ± standard deviation in µg g^{-1} (n = 9) and the values in parenthesis correspond to the agreement with reference values.

Samples	MIC-DV	MAD-SRC
CNT-1	15392 ± 347 (96%)	15188 ± 1458 (97%)
CNT-2	19916 ± 1022 (104%)	19892 ± 833 (97%)
CRM 2LV-BIO-SWCNT-1[*]	14303 ± 1203 (99%)	ND

[*]Certified value: 14400 ± 800 µg g^{-1}; ND = not determined.

3.3 Green aspects of the proposed colorimetric smartphone-based method

A new tool, named White Analytical Chemistry (WAC)[44] was used to evaluate the green and sustainability aspects of the proposed method and reference methods used

for Ni determination in CNT. The WAC used the RGB (not related to the colorimetric purposes described in this word) colors to demonstrate the environmental impact of analytical methods. The data considered for this evaluation are presented in Figure S2 (see supporting information). The results for WAC evaluation of proposed method MIC-DV/SBC and referential method MAD-SRC/ICP-OES are shown in the Figure S3 (see supporting information).

For red principles (analytical performance) results, all the methods achieved 100% in the red attribute. This value was considered once all the methods showed excellent analytical performance for Ni determination in CNT. Therefore, considering green principles (green chemistry) results for MAD-SRC/ICP-OES method presented the lowest value (79.2%), ruled by the amount of water and reagent generated. For these calculations, the reagent required for the calibration curve, as well as for all the reagents used during the combustion/digestion process were considered.

The lowest blue principles (practical side) results (53.8%) were obtained for the reference method, which is related to the cost-efficiency and time-efficiency, assessed at the score of 60 and 50, respectively. The commercial MAD-SRC/ICP-OES system presents a relatively high acquisition cost comparing to the MIC-DV/SBC system. In summary, the MIC-DV/SBC method, when compared to the MAD-SRC/ICP-OES, presented the closest value to 100% (95.6%) for the whiteness parameter Figure S4 (see supporting information). Meanwhile, the MAD method showed value of 77,6% for the whiteness parameter.

The whiteness is an easily interpretation indicator to assess which method should be chosen to be used. However, the other attributes such as the values for green, blue and red must also be evaluated, since they describe some important criteria such as LOQ, accuracy and cost-effectiveness of the method.[44] Therefore, it is possible to observe that

the proposed method using MIC-DV/SBC combined with a smartphone-based colorimetric Ni determination proved to be in all evaluation criteria. This method proved to be analytically suitable for Ni determination in CNT, in addition to being functional, inexpensive and in agreement with the principles of GAC[1].

4. CONCLUSIONS

In this study a method for colorimetric Ni determination in CNT by USB camera coupled to a smartphone combined to MIC-DV as sample preparation was proposed. A good agreement between MIC-DV and MAD as a conventional sample preparation method was achieved, allowing the Ni determination by both ICP-OES, and proposed colorimetric method (SBC). The MIC-DV digests showed relatively low dissolved carbon content, showing that the digests are suitable for elements determination by spectrometric techniques.

ASSOCIATED CONTENT

Supporting Information

Figure S1. Effect of system pressurization in MIC-DV for Ni determination in CNT-1. Conditions: 5 mg of CNT-1, 5 mg of NH_4Cl, 5 mL of absorbing solution (HNO_3: HCl (1:1)), 40 μL of NH_4NO_3 10 mol L^{-1}. The bars represent the agreement (%) with the reference values (MAD-SRC/ICP-OES) and the error bars represent the standard deviation (n = 5).

Figure S2. Data used for the methods evaluation according to the red, green, and blue principles using the RGB 12 algorithm.

Figure S3. Comparison between Ni determination in CNT by MIC-DV/SBC and MAD-SRC/ICP-OES according to the WAC principles.

Figure S4. Main assessment outcomes obtained from the WAC analysis; White line indicates 100% of the appropriateness for Ni determination in CNT.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Supporting Information

Contents

Figure S1. Effect of system pressurization in MIC-DV for Ni determination in CNT-1. Conditions: 5 mg of CNT-1, 5 mg of NH_4Cl, 5 mL of absorbing solution (HNO_3: HCl (1:1)), 40 µL of NH_4NO_3 10 mol L^{-1}. The bars represent the agreement (%) with the reference values (MAD-SRC/ICP-OES) and the error bars represent the standard deviation (n = 5).

Figure S2. Data used for the methods evaluation according to the red, green, and blue principles using the RGB 12 algorithm.

Figure S3. Comparison between Ni determination in CNT by MIC-DV/SBC and MAD-SRC/ICP-OES according to the WAC principles.

Figure S4. Main assessment outcomes obtained from the WAC analysis; White line indicates 100% of the appropriateness for Ni determination in CNT.

Figure S1. Effect of system pressurization in MIC-DV for Ni determination in CNT-1. Conditions: 5 mg of CNT-1, 5 mg of NH_4Cl, 5 mL of absorbing solution (HNO_3: HCl (1:1)), 40 μL of NH_4NO_3 10 mol L^{-1}. The bars represent the agreement (%) with the reference values (MAD-SRC/ICP-OES) and the error bars represent the standard deviation (n = 5).

RED PRINCIPLES (analytical performance)			R1: Scope of application	R2: LOD and LOQ			R3: Precision			R4: Accuracy		
	Method number	Method name	0-100	LOD	LOQ	0-100	RSD% (repeatability)	RSD% (reproducibility)	0-100	Relative error (%)	Recovery (%)	0-100
	1	MIC-DV/SBC	100	35 µg g^{-1}	135 µg g^{-1}	100	6-9%	not determined	100	not determined	96-104%	100
	2	MAD-SRC/ICP-OES	100	1.80 µg g^{-1}	6.1 µg g^{-1}	100	4-5%	not determined	100	not determined	97%	100

GREEN PRINCIPLES (green chemistry)			G1: Toxicity of reagents (impact and biodegradation)		G2: Amount of reagents and waste			G3: Concumption of energy and other media	G4: Direct impacts (safety, use of animals and GMOs)		
	Method number	Method name	Total number of pictograms	0-100	Reagent consumption	Waste production	0-100	1-100	Occupational hazards	Safety of users (0-100)	Use of animals (0 if no, 1 if yes)	Use of GMO (0 if no, 1 if yes)
	1	MIC-DV/SBC	13	60	correlated with waste	55 mL/per sample	100	100	10	60	0	0
	2	MAD-SRC/ICP-OES	5	100	correlated with waste	530 mL/per sample	40	80	6	85	0	0

BLUE PRINCIPLES (practical side)			B1: Cost-efficiency		B2: Time-efficiency		B3: Requirements			B4: Operational simplicity		
	Method number	Method name	Total cost	0-100	Speed of analysis	0-100	Sample consumption	Sample consumption (0-100)	Other needs: advanced instruments, skills,	Miniaturization (0-100)	Integration and automation (0-100)	Portability (0-100)
	1	MIC-DV/SBC	extremely low	100	extremely low	100	5 mg/per sample	100	100	100	100	100
	2	MAD-SRC/ICP-OES	moderate	60	moderate	50	25 mg/ per sample	80	50	40	40	40

Figure S2. Data used for the methods evaluation according to the red, green, and blue principles using the RGB 12 algorithm.
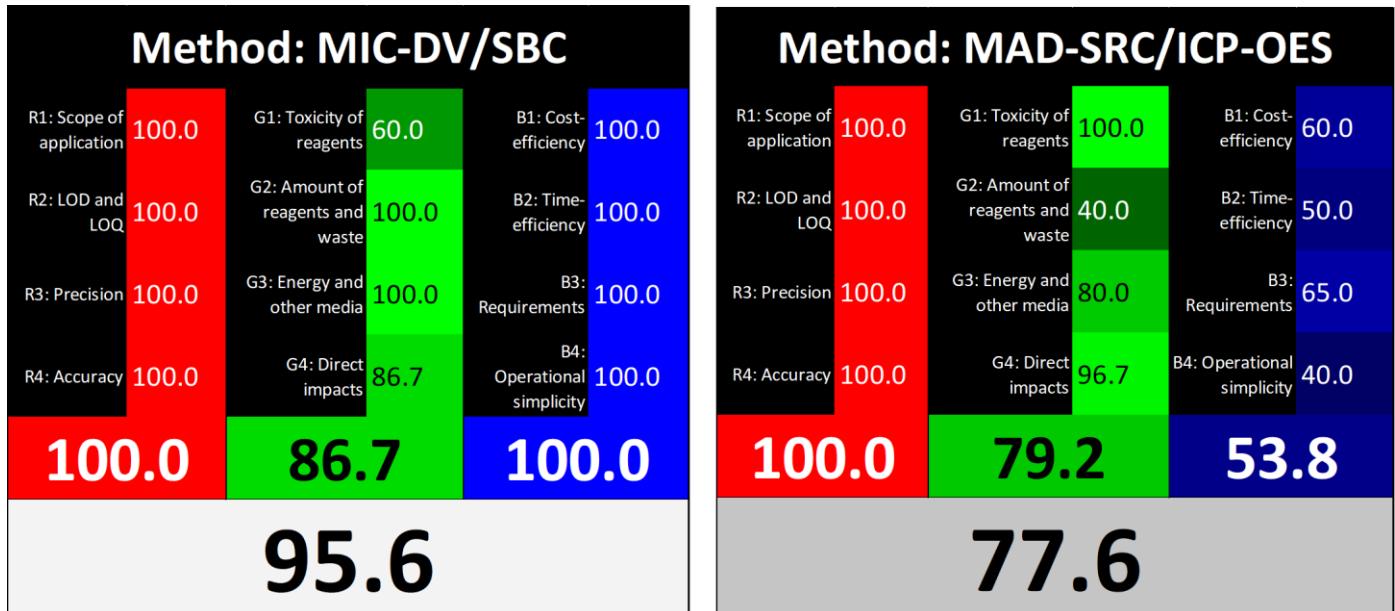
**Figure S3.** Comparison between Ni determination in CNT by MIC-DV/SBC and MAD-SRC/ICP-OES according to the WAC principles.

Manuscrito 2: **Lanthanum determination in carbon nanotubes**

by using microwave-induced combustion in disposable vessels

as a green approach for hard-to-digest samples

Manuscrito formatado para submissão ao periódico Talanta

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Lanthanum determination in carbon nanotubes by using microwave-induced combustion in disposable vessels as a green approach for hard-to-digest samples

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Abstract

The digestion of carbon nanotubes (CNT) is still a challenge matrix to be digested due to its refractoriness, requiring the use of large amounts of reagents to ensure the complete digestion, as well as longer reaction times. In this way, a fast, simple, low-cost, and effective sample preparation protocol for CNT digestion based on the new microwave-induced combustion in disposable vessels (MIC-DV) method for further La determination was proposed. For the CNT combustion, polypropylene vessels containing the quartz holder and sample were placed in a metallic rotor which was inserted into the cavity of a domestic microwave oven. To achieve good analytical performance, some parameters of MIC-DV such as sample mass and type and concentration of absorbing solution were optimized. For results comparison, CNT samples were also digested by microwave-assisted digestion (MAD) and microwave-induced combustion (MIC), with agreements ranging from 92 to 99% and relative standard deviation below 8%. Lanthanum was determined by inductively coupled plasma mass spectrometry (ICP-OES). The La concentration in the two analyzed samples ranged from 18.8 to 19.6 µg g^{-1} and the limit of quantification was 1.3 and 3.5 µg g^{-1}, combing MIC-DV with ICP-OES. To evaluate the green and sustainability aspects of the proposed method and reference methods, a new tool, named White Analytical Chemistry (WAC) was used. According to these features, the proposed MIC-DV method could be considered as a promising and greener (21.6% more than MIC) alternative for elemental quality control in CNT.

Keywords: carbon nanotubes, sample preparation, MIC-DV, lanthanum, ICP-OES.

5. INTRODUCTION

Most of the detection techniques, except the direct solid analysis samples ones, require the conversion of solid matrices to a solution compatible with the analytical instrument. The sample preparation step aims the conversion of the analyte into a suitable form to be quantified by the chosen technique [1]. Considering the diversity of matrices that need to be analyzed, it is necessary to develop new sample preparation methods that are effective for different types of samples [1]. The choice of sample preparation method will depend on the matrix characteristics, the analyte to be determined, as well as its concentration, detection technique and, finally, the desired accuracy and precision [2].

The digestion in closed systems using microwave radiation as energy source have proven to be an efficient, fast and safe choice for preparing different sample matrices, such as biological [3, 4], botanical [5], fuel [6], polymer [7], among others. Microwave-assisted digestion (MAD) in closed vessels has been considered the state of the art for sample preparation, because its high heating rates reduce the digestion time and the use of closed vessels minimizes the risks of analyte losses and contamination [8, 9]. However, for complex matrices as carbon nanotubes (CNT), the digestion for subsequent element determination is not an easy task but present a great potential for application [10, 11]. It should be noted that some limitations for the use of MAD for CNT digestion have been reported in the literature [11], mainly because the inertness of such materials. In addition, there is a limitation regarding to the sample mass to be digested, requiring the use of greater amounts of reagents and a longer digestion time [11-13].

In the last two decades, the use of microwave radiation combined and used for starting the ignition in combustion reactions has been widely applied and the microwave-induced combustion (MIC) is the most striking example [14-16]. MIC combines the advantages of the MAD methods with those of combustion ones in closed (and eventually

opened) vessels [17]. The main advantage of MIC is the high digestion efficiency of organic matrices, even those that are hard to digest [15, 18] , as well as inorganic matrices [7, 16, 19, 20]. In addition, diluted (acid, neutral or alkaline) absorbing solutions can be used, reducing the amount of reagents and the risk of contamination [17].

After almost twenty years from the first publication about MIC [19], it has been successfully applied to different matrices, mainly those with high carbon content, such as combustibles [21], polymers [22, 23] and CNT [24, 25]. Although excellent results can be achieved using MIC, it presents a disadvantage related to the cost involved for instrument acquisition and maintenance. In this context, the microwave-induced combustion in disposable vessels (MIC-DV) was recently proposed as an alternative [26]. MIC-DV consists of using a domestic microwave oven and polypropylene (PP) disposable vessels, where only the quartz holder can be reused [26, 27].

Considering the development of a simple, fast, and low-cost method, this work proposes the use of MIC-DV as a sample preparation approach for CNT digestion and further La determination by inductively coupled plasma optical emission spectrometry (ICP-OES). The parameters of MIC-DV that were not adapted from the literature were optimized, such as the volume and concentration of absorbing solution, and pressure applied into the disposable vessels. The results were compared with those from CNT digestion by MAD and MIC, followed by La determination by ICP-OES.

6. EXPERIMENTAL

6.1 Instrumentation

The CNT pellets (5 to 20 mg) were prepared using a hydraulic press (Specac) set at 1 ton (1 min). The proposed MIC-DV system consists of a domestic microwave oven (BMK38LQBNA, Brastemp, Brazil), equipped with a lab-made aluminum rotor for

supporting the PP vessels (50 mL, Sarstedt, Germany). The quartz holders were also produced at the Chemistry Department of Universidade Federal de Santa Maria. For pressurizing the vessels with oxygen, a capillary tube (3.5 mm O.D., 2.5 mm I.D., 150 mm of length, made of perfluoroalkoxy alkane) was connected to a flowmeter (FR 2000 series, Key Instruments, USA). The details of the system are shown in Figure 1.
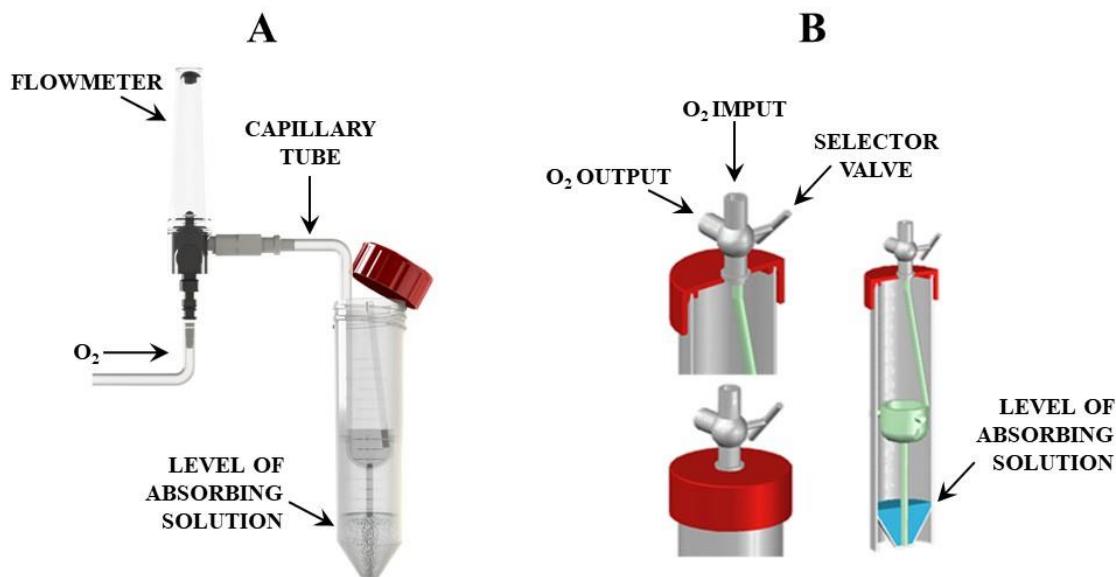

Figure 1. Proposed MIC-DV system for sample digestion using purged and pressurized approaches. A) Vessel purging apparatus (flowmeter and capillary tube). B) Vessels pressurizing apparatus (selector valve and hole for oxygen input and output).

For results comparison, CNT were also digested by MAD in a single reaction chamber (MAD-SRC) system. The experiments were carried out using a microwave sample preparation system (Ultrawave™, Milestone, Italy) equipped with 12 quartz vessels (total volume of each vessel of 15 mL) and a 1 L microwave cavity made of stainless steel with a polytetrafluoroethylene cover. The maximum operational temperature and pressure were set at 270 °C and 160 bar, respectively. The SRC chamber was previously filled with 120 mL of water and 5 mL of HNO_3 14.4 mol L^{-1} and was

pressurized with argon (99.996%, White Martins, Brazil) up to 40 bar before the microwave irradiation. The vessels were irradiated with a maximum power of 1500 W.

The results were also compared by using MIC and La determination by ICP-OES. The experiments were carried out using a microwave sample preparation system (Multiwave 3000, Anton Paar, Austria) equipped with 8 high pressure quartz vessels and quartz holders for sample introduction into the quartz vessels. The quartz vessels present an internal volume of 80 mL and maximum operational pressure of 80 bar. The operational conditions of conventional MIC were adapted from a previous work [24].

An inductively coupled plasma optical emission spectrometer (Spectro Ciros CCD, Spectro Analytical Instruments, Germany) equipped with a cross-flow nebulizer coupled to a Scott double-pass spray chamber was used for C and La determination in the digests. The operational conditions were radiofrequency power of 1400 W; argon flow rate for plasma, auxiliary and nebulizer gases were 12, 1.0, and 1.00 L min^{-1}, respectively. Emission lines were set at 408.672 nm for La, 193.091 nm for C and 371.030 nm for Y (monitored as internal standard for C determination).

6.2 Samples, standards and reagents

Two commercial CNT samples were acquired from a nanomaterials producer (USA), which were identified as CNT-1 and CNT-2. CNT-1 is functionalized with COOH groups and present 95% of minimum purity and 1.47-1.63% of mass fraction. CNT-2 is functionalized with OH groups and present 95% of minimum purity and 2.36 to 2.60% of mass fraction.[27] Before weighing the CNT (including for pellets preparation) for MIC-DV, MAD and MIC, the samples were oven dried (Nova Ética, Brazil) at 105 ℃ for 120 min. Sample CNT-1 was used for the optimization of the proposed method.

A Milli-Q water purification system (Direct-Q 3 UV, 18.2 MΩ cm, Millipore Corp., USA) was used and water was used for preparing all the solutions. Nitric acid (65%, 1.4 kg L^{-1}, 14.4 mol L^{-1}, Merck) used for sample digestion was distilled in a sub-boiling distillation system (model duoPUR, Milestone). Hydrochloric acid (37%, 1.19 kg L^{-1}, Merck) was also distilled in the sub-boiling system.

Ammonium nitrate (Merck, Germany) was prepared by dissolving the salt in ultrapure water and used as igniter in MIC-DV and MIC systems. This solution was used by pipetting it in filter paper discs with low ash content (Black Ribbon Ashless, Schleicher & Schüll GmbH, Germany), which were used as combustion aid. The paper discs were previously cleaned using 1.4 mol L^{-1} HNO$_3$ for 20 min in an ultrasonic bath (P120H, 330 W, Elmasonic, Germany) set at 37 kHz. After sonication, paper discs were rinsed with ultrapure water and dried in a class 100 laminar flow bench (CSLH-12, Veco, Brazil). Oxygen (99.6%, White Martins-Praxair) was used for purging or pressurization of MIC-DV and MIC systems.

For the determination of dissolved carbon in digests by ICP-OES, a carbon stock reference solution (1000 mg L^{-1} C) from citric acid (Merck, Germany) was prepared in water. Reference solutions for instrument calibration were prepared form the stock solution by serial dilution, reaching concentrations from 5 to 500 mg L^{-1}. Yttrium (1000 mg L^{-1}, Spex, USA) was added as internal standard in the samples, standards, and blanks at final concentration of 1 mg L^{-1}. For the measurements by ICP-OES, the reference solutions were prepared by dilution of a 10 mg L^{-1} multielement stock solution (SCP 33MS, SCP Science, Canada) in 0.7 mol L^{-1} HNO$_3$, with concentration ranging from 2.5 to 500 µg L^{-1}. Argon (99.996%, White Martins) was used for the measurements by ICP-OES.

6.3 Microwave-induced combustion in disposable vessels

The procedure for MIC-DV was performed as previously described in the literature [28, 29], where the filter paper, previous cleaned, was placed on the quartz holder and 40 μL of 10 mol L^{-1} NH$_4$NO$_3$ solution were added. The sample as pellet was weighed and placed over the filter paper positioned on the quartz holder. Previously to the insertion of holder + paper + sample, the absorbing solution was transferred to the PP vessel. It is important to mention that the cover of PP vessels was adapted for pressurization with oxygen. Thereafter, the vessels were closed and inserted in the metallic rotor and then into the microwave oven cavity. The vessels were irradiated with maximum power for about 30 s, up to all the vessels start the combustion. Immediately after stopping the irradiation, the vessels were removed from the metallic rotor and manually shaken for La absorption. After 1 min shaking, the vessels were opened, and the quartz holder was removed. For cleaning, the quartz holder was immersed in a glass beaker containing 7 mol L^{-1} HNO$_3$ solution, which was maintained under boiling for 30 min in a hotplate.

For the MIC-DV optimization, sample CNT-1 was used. The sample mass that could be burned in the MIC-DV system was evaluated as a function of the residue remaining in the quartz holder and in the digest. Therefore, the sample mass to be burned was chosen according to the qualitative experiments previously performed (data not shown). The type of absorbing solution by using H$_2$O and HNO$_3$ at 1, 3, 5, 7 e 14 mol L^{-1}, as well as its volume (1.0, 2.0 and 5.0 mL) were also optimized.

6.4 Microwave-assisted digestion

The MAD-SRC was used as a reference method for results comparison with those from MIC-DV. The conditions for MAD-SRC method were adapted from the literature

[11] and the digestions were carried out using the following conditions: 25 mg of CNT and 6 mL of 14.4 mol L^{-1} HNO_3 + 0.5 mL of 30% H_2O_2 as digestion solution. The SRC chamber was filled with 120 mL of water and 5 mL of concentrated HNO_3, which was further pressurized with argon up to 40 bars before the irradiation program. The microwave irradiation program was: *i)* ramp of 10 min up to 180 °C and hold for 15 min at 180 °C, *ii)* ramp of 5 min up to 270 °C and hold for 35 min at 270 °C and *iii)* 40 min at 40 °C for cooling. After cooling, the pressure was released, the digests were transferred to PP vessels and diluted with ultrapure water up to 20 mL. Lanthanum was determined by ICP-OES in the digests.

6.5 Microwave-induced combustion

For MIC, the experimental conditions were adapted from a previous work [24]. Pellets of 400 mg of CNT were prepared using a hydraulic press, applying 2 ton for 1 min. After weighing, the samples were placed on the filter paper positioned over the quartz holder and 50 µL of 6 mol L^{-1} NH_4NO_3 solution were added to the filter paper. As absorbing solution, 6 mL of a mixture of HNO_3 and HCl (1:1) both concentrated was added into the digestion vessel. The quartz vessels containing the absorbing solution and the quartz holder + CNT were pressurized with 20 bar of oxygen and the rotor was placed inside the cavity of the microwave oven. The microwave irradiation program was: *i)* 1 min at 1400 W (sample combustion), *ii)* 15 min at 1400 W (reflux) and *iii)* 20 min at 0 W (cooling). After cooling, the pressure of vessels was released, the digests were transferred to PP vessels, diluted with ultrapure water up to 25 mL and La was determined by ICP-OES.

The limit of detection (LOD, 3σ) and the limit of quantification (LOQ, 10σ) values for all the methods (MIC-DV, MAD-SRC and MIC, all using ICP-OES as detector) were calculated considering the average of the blanks according to Eurachem Guide [30].

The data were evaluated using analysis of variance (ANOVA, one-way) followed by student's t-test with 5% of significance level using Statistica 5.1 software (Statsoft, 2004, USA).

7. RESULTS AND DISCUSSION

7.1 MIC-DV optimization

Initially, for obtaining a reference value for La concentration, CNT-1 was digested by MIC as previously described and La was determined by ICP-OES. The La concentration found in CNT-1 was $20.1 \pm 1.0\ \mu g\ g^{-1}$ and this value was used for agreement calculation (showed in some figures) during the MIC-DV optimization.

Initially, it was necessary to investigate the most suitable sample mass to be burned in the MIC-DV system. Considering the previous results achieved by our research group for CNT digestion by MIC-DV (data not published yet), experiments were carried out using the pressurized system. Sample masses of 5, 10, 15 and 20 mg was evaluated, but the combustion was not complete (presence of suspended solids in solution and sample particles on the quartz support) using 15 and 20 mg of CNT. Therefore, considering the low La concentration in the samples, 10 mg were selected for further experiments.

The influence of the volume of absorbing solution on La recovery using MIC-DV was evaluated. Therefore, volumes of 1.0, 2.5 and 5.0 mL of absorbing solution (1 mol L^{-1} HNO_3) were evaluated and no statistical difference (Student's t-test, $p > 0.05$) was observed among the studied volumes. For all evaluated solutions, recoveries of about 70%

were achieved. It should be highlighted that the volume of 1 mL was not chosen due to the low volume available for the determination by ICP-OES, which requires at least 1.5 mL for the measurement in triplicate. Therefore, 2.5 mL of absorbing solution was used in subsequent experiments.

The influence of the type of absorbing solution and its concentration on La recovery also was evaluated, by using water and diluted HNO_3 (1, 3, 5, 7 and 14 mol L^{-1}). The results are shown in Figure 2.
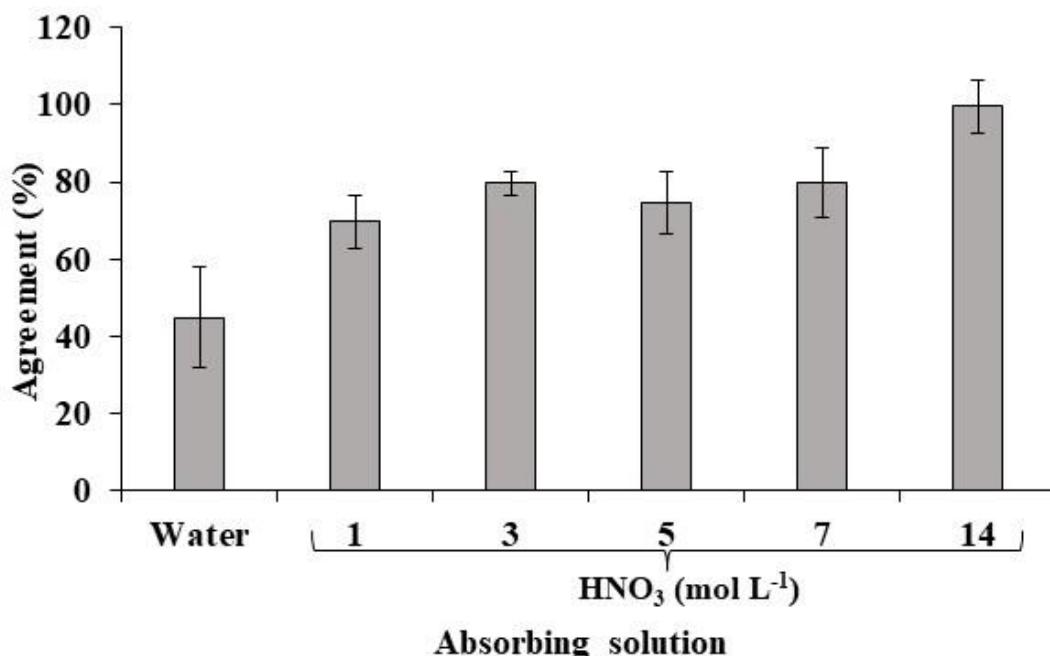

Figure 2. Influence of absorbing solution for MIC-DV and La determination by ICP-OES. Conditions: 10 mg of CNT-1, 2.5 mL of absorbing solution, 40 μL of NH_4NO_3 10 mol L^{-1} and pressurization with up to 1 bar of oxygen. The bars represent the agreement (%) with the reference values (MIC/ICP-OES) and the error bars represent the standard deviation (n = 5).

As can be seen in in Figure 2, when HNO_3 14 mol L^{-1} was used, the agreement for La reached 99% and no statistical difference (Student's t-test, $p > 0.05$) was observed between the results from the proposed method (MIC-DV) and reference method (MIC)

[24]. Considering the results from the literature, some metallic contaminants (*e.g.*, La) may be present into the CNT structure, requiring the complete matrix digestion to achieve quantitative La recoveries, as well as in combination of using higher HNO_3 concentration.

Although CNT are mainly composed by carbon, its digestion even by combustion methods is not an easy task [24]. Thus, the oxygen pressure applied to the MIC-DV system and its influence on La recovery were evaluated. The results are shown in Figure 3.
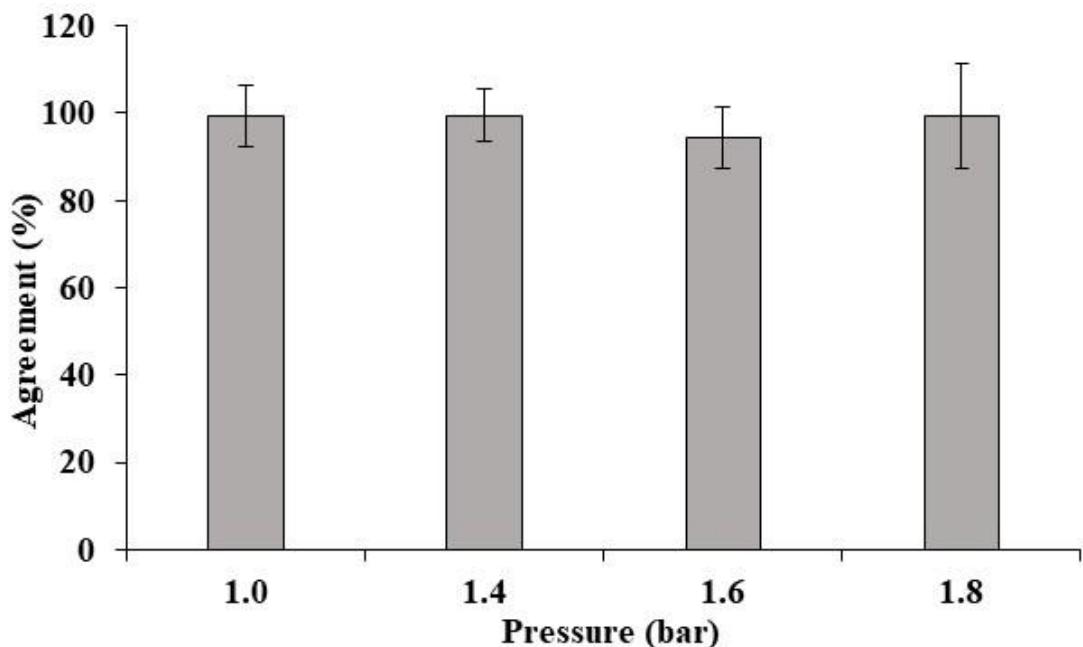
Figure 3. Influence of oxygen pressure applied to the MIC-DV in La determination by ICP-OES. Conditions: 10 mg of CNT-1, 2.5 mL of absorbing solution and 40 μL of NH_4NO_3 10 mol L^{-1}. The bars represent the agreement (%) with the reference values (MIC/ICP-OES) and the error bars represent the standard deviation (n = 5).

In the initial experiments, the purged system was evaluated (results not showed), but no more than 5 mg were able to be completely burned. In the pressurized system, however, it was possible to burn up to 10 mg of sample and good agreement (higher than

95%) was obtained with the reference method (MIC) and no statistical difference (Student's t-test, $p > 0.05$) was observed when different oxygen pressures were applied to pressurize the system. According to Schmidt *et. al.* [31], it is possible to calculate the stoichiometric oxygen amount required for the complete burning of a specific sample mass. Therefore, according to the results when 1 bar of oxygen was applied to the MIC-DV system for burning of 10 mg of CNT, corresponding to an excess of about 59% of oxygen. This excess can explain why by increasing the oxygen amount did not impact on La results. It is important to mention that hard to digest samples requires an excess of about 30%. Therefore, for subsequent experiments, a pressure of 1.0 bar of oxygen was applied, to assure an excess of oxygen in the MIC-DV system. It should be mentioned that the purged system was no used because no more than 5 mg were completely burned and no showed suspended solids in solution (data not shown).

The dissolved carbon after MIC-DV was also determined under optimized conditions (10 mg of sample mass, 2.5 mL of absorber solution and 1.0 bar of oxygen). The dissolved carbon was determined by ICP-OES and the concentration in the digest was below 500 mg L^{-1}. According to the literature [32], carbon concentration less than 5000 mg L^{-1} does not cause spectral interference on La determination by ICP-OES.

7.2 Lanthanum determination in CNT

The optimized conditions of MIC-DV were applied for the digestion of CNT for further La determination by ICP-OES. Thus, two samples (CNT-1 and CNT-2) were digested by MIC-DV, MIC and MAD-SRC and results are shown in Table 1.

Table 1. Results for La determination by ICP-OES in CNT samples after digestion by MIC-DV, MIC and MAD-SRC. Results ($\mu g\ g^{-1}$) represent the mean $\pm$ standard deviation, n=3.

Sample	MIC-DV	MIC	MAD-SRC
CNT-1	19.6 ± 1.3	20.1 ± 1.0	21.3 ± 1.5
CNT-2	18.8 ± 1.6	20.2 ± 1.2	19.0 ± 1.4

The results for La were considered statistically similar for all the sample preparation methods applied. Comparing the results achieved by MIC-DV/ICP-OES, the agreement for both samples ranged from 92 to 99%, when compared to MIC and MAD-SRC. In addition, the relative standard deviation (RSD) values for MIC-DV were below 8%, which were considered as acceptable considering the difficulties concerning to the CNT digestion. In addition, the proposed method overcomes some limitations presented by CNT digestion proposed in the literature [8, 11, 13, 33], such as the long sample preparation time and the use of large amounts of reagents, as well as the mixing of reagents for the complete matrix digestion.

Considering the previous works for CNT digestion and the complexity to obtain the complete digestion of this type of matrix, the proposed method can be considered as a simple alternative for further La determination. Furthermore, the LOD and LOQ values for MIC-DV/ICP-OES were 1.3 and 3.5 μg g^{-1}, respectively. The LOQ value can be considered relatively low and fit for purpose for the La determination in CNT. In addition, even using a low-pressure and small system, the sample mass applied can be compared with the previous works in the literature [11, 24].

7.3 Green aspects of MIC-DV

Since the conception of MIC-DV, the main advantage was linked to its performance under the aspects of the green analytical chemistry (GAC) [34], more recently, to the White Analytical Chemistry (WAC) [35]. The WAC is a new tool that

allow to evaluate the analytical methods considering the sustainability aspects, which was proposed by splitting the 12 GAC principles in three categories, considering the RGB colors.

Thus, the performance of MIC-DV on WAC parameters was compared with MIC and MAD-SRC, all using ICP-OES as detection technique, which is shown in Figure 5. The data for the calculations using WAC are presented in Figure S1 (see Supplementary Material).
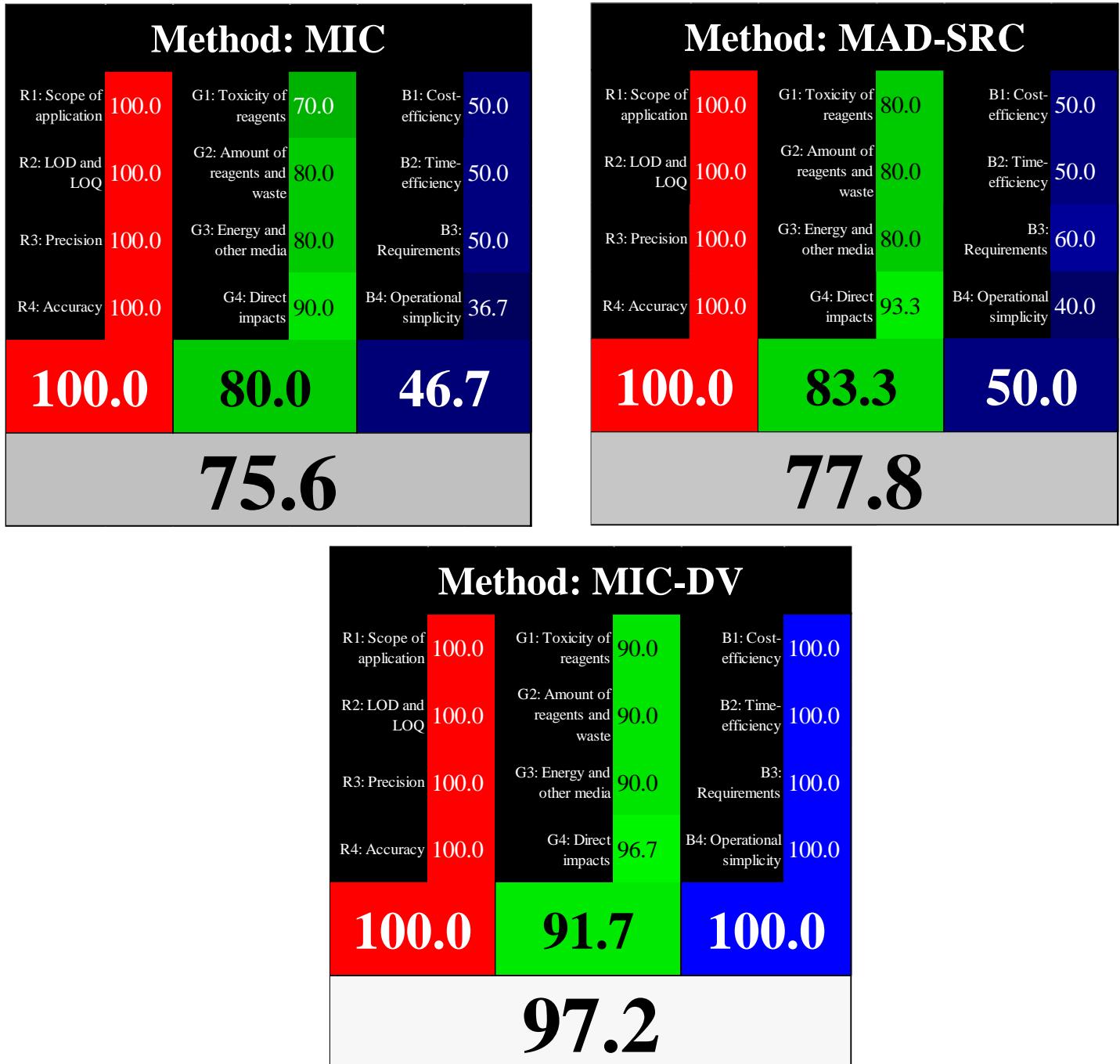
Figure 5. Comparison of sample preparation methods based on WAC criteria for La determination in CNT.

According to the results from WAC parameters, all the methods present excellent analytical performance (100% in the red attribute). The graph obtained through the results

shown in Fig. 5 can be found in the Figure S2 (Supplementary Material). Considering the "green" aspects, the volume of waste generated was similar (from 80.0 to 91.7% in the green attribute) for all the methods, since the waste generated also considered the preparation of the calibration curve for La determination by ICP-OES, minimizing the effect of the digest volume. However, if only the digest volume was considered, the MIC-DV is advantageous, as there is no need of dilution after digestion and previously the measurement. Considering the final volume of the digest, for MIC-DV it was only 2.5 mL, while for MAD and MIC the volumes were 20 and 25 mL, respectively. In addition, MIC-DV required only HNO_3 for La absorption, whereas the other methods need to use H_2O_2 and HCl for a quantitative La recovery. All the advantages presented by the proposed method are in line with the principles of GAC. [34, 36] Considering the methods performance concerning to the cost and efficiency, MIC-DV showed a great advantage. According to Duarte *et al.*,[26] the cost to manufacture a complete MIC-DV system is less than US\$ 200, which is at least 500 times lower than commercial systems (*e.g.*, MAD-SRC and MIC). In addition, MIC-DV is time-saving, requiring about 10 min for 5 simultaneous combustions, mainly because the reflux step is not allowed as in MIC method. However, the inability to perform a reflux step can be considered as a disadvantage, considering the analytical aspects. It is also worth highlighting the safety aspects presented by the proposed MIC-DV method, since the flask reaches a maximum pressure of 2 bar and a low volume of acid is used as absorbing solution.[26]

8. CONCLUSIONS

The MIC-DV allowed the development of a simple, fast, and low-cost method for the digestion of an extremely hard to digest sample as CNT. Lanthanum was determined by ICP-OES after MIC-DV with suitable LOQ and in agreement with the principles of

WAC. The volume of sample and reagents were significantly reduced comparing to the conventional methods, as well the environmental impacts generated, and the cost of analysis were reduced. Considering all the advantages of the proposed MIC-DV mainly in terms of cost and efficiency, it can be a suitable alternative for routine CNT analysis for trace elements determination.

DECLARATION OF COMPETING INTEREST

The authors declare no competing financial interest.

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Supplementary material

Contents

Figure S1. Data used to evaluation methods according to the red, green, and blue principles using the RGB 12 algorithm.

Figure S2. Main assessment outcomes obtained from the WAC analysis; White line indicates 100% of the appropriateness for La determination in CNTs.

RED PRINCIPLES (analytical performance)

Method number	Method name	R1: Scope of application 0-100	R2: LOD and LOQ LOD	LOQ	0-100	R3: Precision RSD% (repeatability)	RSD% (reproducibility)	0-100	R4: Accuracy Relative error (%)	Recovery (%)	0-100
1	MIC-DV	100	1.30 µg g^{-1}	3.50 µg g^{-1}	100	7-8%	not determined	100	not determined	92-99%	100
2	MIC	100	0.50 µg g-1	1.50 µg g-1	100	5-6%	not determined	100	not determined	94-106%	100
3	MAD	100	0.95 µg g-1	3.00 µg g-1	100	7%	not determined	100	not determined	94-106%	100

GREEN PRINCIPLES (green chemistry)

Method number	Method name	G1: Toxicity of reagents (impact and biodegradation) Total number of pictograms	0-100	G2: Amount of reagents and waste Reagent consumption	Waste production	0-100	G3: Consumption of energy and other media 1-100	Occupational hazards	G4: Direct impacts (safety, use of animals and GMOs) Safety of users (0-100)	Use of animals if no, 1 if yes	(0 Use of GMO (0 if no, 1 if yes)
1	MIC-DV	3	90	correlated with waste	507.5 mL/per sample	90	90	3	90	0	0
2	MIC	5	70	correlated with waste	530 mL/per sample	80	80	7	70	0	0
3	MAD	4	80	correlated with waste	530 mL/per sample	80	80	6	80	0	0

BLUE PRINCIPLES (practical side)

Method number	Method name	B1: Cost-efficiency Total cost	0-100	B2: Time-efficiency Speed of analysis	0-100	B3: Requirements Sample consumption	Sample consumption (0-100)	Other needs: advanced instruments, skills, facilities (0-100)	B4: Operational simplicity Miniaturization (0-100)	Integration and automation (0-100)	Portability (0-100)
1	MIC-DV	extremely low	100	extremely low	100	10 mg/per sample	100	100	100	100	100
2	MIC	high	50	moderate	50	400 mg/per sample	60	40	30	40	40
3	MAD	moderate	50	moderate	50	25 mg/ per sample	80	40	40	40	40

Figure S1. Data used to evaluation methods according to the red, green, and blue principles using the RGB 12 algorithm.
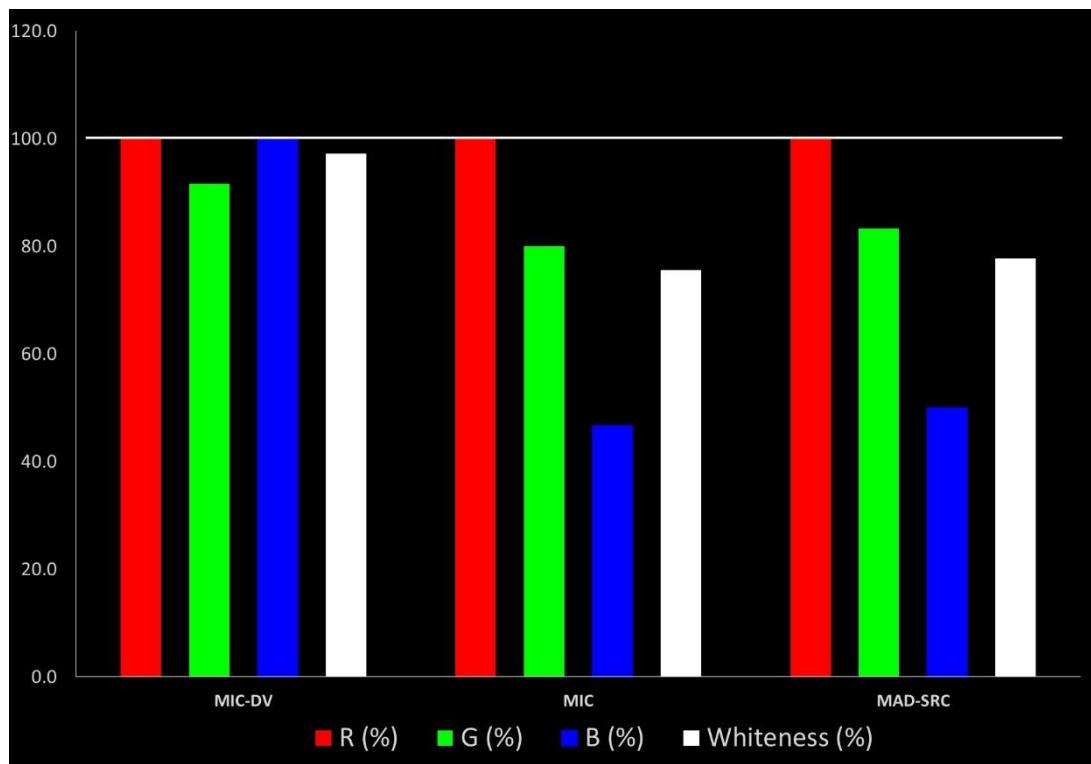
Figure S2. Main assessment outcomes obtained from the WAC analysis; White line indicates 100% of the appropriateness for La determination in CNTs.

4 DISCUSSÃO GERAL

Os resultados obtidos no presente trabalho, demonstram que a combustão iniciada por micro-ondas em frascos descartáveis (MIC-DV) é uma alternativa viável, que apresenta muitas vantagens para a decomposição de amostras de nanotubos para posterior determinação elementar. A simplicidade na utilização, o baixo custo do sistema da MIC-DV e os resultados obtidos, juntamente com o uso de técnicas de determinação elementar de baixo custo e portáteis como os *smartphones*, demonstram ser uma alternativa promissora frente aos métodos convencionais (MIC/ICP-OES e MAD-SRC/ICP-OES).

De modo a obter as melhores condições de análise, métodos estatísticos foram empregados de modo a avaliar os melhores parâmetros para cada ensaio. No manuscrito 1, para o método de preparo de amostra foram avaliadas a influência da massa de amostra, do volume de solução absorvedora, concentração da solução e pressão aplicada no frasco de combustão. Nas queimas realizadas empregando o sistema da MIC-DV, pode-se observar que quando foi utilizada massa de 5 mg de amostra, sistema pressurizado (1 bar de O_2) e solução absorvedora composta por HNO_3:HCl (1:1) a queima foi completa, não restando sólidos na solução. Porém, não foi possível obter recuperações superiores a 50% para Ni, sem que fosse utilizado o pellet de NH_4Cl junto do pellet da amostra no momento da queima.

Com base nos resultados obtidos foi possível ajustar as condições de análise de modo a obter resultados satisfatórios, sem diferença estatística significativa dos resultados obtidos por MAD-SRC. Cabe destacar, que na digestão empregando o sistema MAD-SRC é necessária a diluição da amostra, uma vez que se faz necessária a lavagem do frasco reacional no momento da transferência do digerido. Além disso, o tempo total para digestão das amostras foi de 65 minutos, mais o tempo necessário para resfriamento do sistema (aproximadamente 40 minutos). Já para a MIC-DV foi necessário um curto tempo de preparo da amostra, cerca de 10 min para 5 combustões simultâneas, não sendo necessário longos tempos de refluxo da solução para que ocorra a completa recuperação do analito.

Para a aplicação da MIC-DV como método de preparo de CNT para posterior determinação de La (Manuscrito 2), os resultados obtidos também foram satisfatórios sem diferença estatística significativa dos resultados obtidos por MAD-SRC e por MIC. Destaca-se, que nas queimas realizadas empregando o sistema da MIC-DV, recuperações

satisfatórias de La foram obtidas com a queima de 10 mg de amostra e emprego de uma solução absorvedora de HNO_3 de 14 mol L^{-1}, não sendo necessário o uso de NH_4Cl. Nestas condições foram obtidos digeridos sem presença de sólidos. Para ambas as condições otimizadas na MIC-DV a queima da amostra ocorreu em aproximadamente 30 segundos após início da aplicação da radiação micro-ondas. Após a combustão, a própria solução absorvedora contida no frasco foi utilizada para lavagem das paredes do frasco e o suporte de quartzo. Sendo assim, não foi necessária a transferência do digerido para outro frasco, bem como a diluição dele, sendo considerada essa etapa uma das grandes vantagens da MIC-DV frente as demais técnicas de preparo de amostras.

Os digeridos obtidos empregando a MIC-DV, se mostraram adequados para determinação de Ni e La por ICP-OES. Além disso, a determinação de Ni também foi feita empregando um sistema colorimétrico de baixo custo. Os resultados para a determinação de Ni por colorimetria não apresentaram diferença estatística significativa dos resultados obtidos por ICP-OES. Como principais vantagens do uso da colorimetria para determinação elementar pode-se citar o baixo custo da técnica, a compatibilidade com a solução absorvedora obtida por MIC-DV, o baixo volume de solução empregada e principalmente a redução do volume de resíduo gerado.

O uso da MIC-DV associado a colorimetria (MIC-SBC), diminuiu significativamente o volume de resíduo gerado, bem como o volume de amostra e reagentes empregados, frente aos métodos convencionais. Essas vantagens citadas fazem com que o método de preparo de amostra proposto esteja em concordância com os princípios da química analítica verde. Além disso, a junção da MIC-DV com a técnica de determinação colorimétrica empregando smartphones possibilitaram o desenvolvimento de métodos adequados para análises de rotina, além de atenderem de modo satisfatório aos princípios da química analítica verde.

5   CONCLUSÃO

Os métodos de análise propostos podem ser considerados uma alternativa viável e promissora para aplicação em análises de rotina para determinação elementar em nanotubos de carbono, visto que se obteve uma boa precisão e exatidão dos resultados frente aos métodos convencionais. O uso da MIC-DV permitiu a aplicação de um sistema de baixo custo e com excelente desempenho para o preparo de amostra, demonstrando características promissoras para sua aplicação em outros tipos de matrizes.

Ao longo de ambos os experimentos a otimização dos parâmetros de análise se mostrou ser uma etapa imprescindível para obter uma melhor resposta e melhorar a precisão dos resultados. Bons resultados foram obtidos a partir do emprego de sistemas de baixo custo, permitindo a determinação de analitos com uma resposta rápida e de forma integrada a sistemas que permitiram análise dos dados de forma simplificada e de fácil operação. Assim, pode se dizer que os métodos propostos se mostraram adequados para análises de rotina, além de atenderem de modo satisfatório aos princípios da química analítica verde.

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