

UNIVERSIDADE TECNOLÓGICA FEDERAL DO PARANÁ

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**AUTENTICAÇÃO DE ORIGEM DO SAL DE COZINHA UTILIZANDO
ESPECTROSCOPIA DE ABSORÇÃO ATÔMICA EM CHAMA E NO
INFRAVERMELHO PRÓXIMO COM INSTRUMENTO PORTÁTIL**

CAMPO MOURÃO

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Authentication of Table Salt Origin Using Flame Atomic Absorption Spectroscopy and
Portable Near-Infrared Spectroscopy

Dissertação apresentada como requisito para
obtenção do título de Mestre em Tecnologia de
Alimentos do Programa de Mestrado em Tecnologia de
Alimentos, da Universidade Tecnológica Federal do
Paraná (UTFPR).

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CAMPO MOURÃO

2025



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Trabalho de pesquisa de mestrado apresentado como requisito para obtenção do título de Mestre Em Tecnologia De Alimentos da Universidade Tecnológica Federal do Paraná (UTFPR). Área de concentração: Tecnologia De Alimentos.

Data de aprovação: 10 de Julho de 2025

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Documento gerado pelo Sistema Acadêmico da UTFPR a partir dos dados da Ata de Defesa em 10/07/2025.

AGRADECIMENTOS

Agradeço primeiramente a Deus, cuja presença me sustentou em cada etapa desta jornada. Foi a fé que me guiou nos momentos de incerteza e me deu forças para persistir com serenidade e propósito.

Sou profundamente grata ao meu orientador, prof. Dr. Evandro Bona, por sua paciência, dedicação e sabedoria. Sua orientação generosa e respeitosa foi essencial não só no aspecto acadêmico, mas também como apoio pessoal.

À minha família, minha eterna gratidão. Ao meu irmão Fabiano, por ser inspiração e incentivo para meu retorno à vida acadêmica. Ao meu pai, cuja memória me acompanha com orgulho, e certamente se sentiria imensamente feliz e honrado com esta conquista. À minha mãe, pelo amor silencioso e constante que me fortaleceu nos bastidores.

Ao meu filho Isaque, minha fonte diária de motivação, e ao meu marido Marlon, por sua paciência, compreensão e apoio incondicional, mesmo nos momentos mais difíceis.

Agradeço também aos colegas do Programa, especialmente à Patrícia, por sua amizade, escuta e presença leve nos momentos exigentes.

Esta conquista representa mais do que um título: é a realização de um sonho adiado por anos. Retorno à academia com maturidade e gratidão à UTFPR, por proporcionar um ambiente de acolhimento, aprendizado e crescimento.

A todos que contribuíram, direta ou indiretamente, o meu mais sincero e carinhoso agradecimento.

Dedico

Ao meu pai, que já não está entre nós, mas continua sendo minha força e inspiração. À minha família, especialmente ao meu marido e ao meu filho, por me darem amor, coragem e motivos para nunca desistir.

RESUMO

O sal de mesa, composto principalmente de cloreto de sódio (NaCl), é utilizado mundialmente como tempero e conservante. Entre os tipos mais comuns estão o sal refinado, o sal marinho, o sal rosa do Himalaia, o flor de sal e o sal *light*. Como sua composição mineral varia conforme a origem geográfica, torna-se possível identificar a sua procedência. Neste estudo, objetivou-se autenticar a origem de sal de mesa de quatro países por meio de espectroscopias de absorção atômica em chama e infravermelho próximo com instrumento portátil. Para tratar os dados obtidos, utilizou-se quimiometria, visando reduzir a dimensionalidade e facilitar a interpretação. A Análise de Componentes Principais (PCA) foi empregada para decompor a matriz original, enquanto o método DD-SIMCA (Modelagem Independente por Analogia de Classe) definiu limites de aceitação no novo espaço a partir das distâncias entre as amostras. Os resultados da espectrometria de absorção atômica em chama (FAAS) revelaram alta variabilidade nos teores de metais entre os países. Observou-se que o sal brasileiro apresentou maior teor de Na, ao passo que o sal francês destacou-se pelos teores elevados de K, Zn, Fe, Mg e Ca. Ao aplicar os modelos DD-SIMCA, o sal do Brasil foi completamente separado dos demais, com apenas cinco erros de classificação, o que comprova que o perfil metálico pode servir como impressão digital para identificar a origem do sal. Já na análise dos espectros NIR, o efeito da origem manifestou-se sobretudo nas regiões de 1 300–1 600 nm (segundo harmônico da água) e abaixo de 1 000 nm (terceiro harmônico). Os modelos DD-SIMCA usando a primeira derivada dos espectros NIR apresentaram 19 erros de classificação para o sal bruto, 23 para o sal seco e apenas 3 para o sal seco e moído. Esses resultados indicam que granulometria e umidade influenciam os espectros, destacando bandas atribuídas à água livre e à água de hidratação; após secagem, as correlações melhoraram para os teores de Mg, Mn e Cu. Por fim, o desempenho dos modelos DD-SIMCA com espectros de amostras secas e moídas foi similar ao obtido com dados de FAAS. Assim, ambas as técnicas FAAS e NIR mostraram-se eficazes na identificação da origem do sal, sendo a NIR uma alternativa mais rápida e de baixo custo, com desempenho comparável ao da FAAS.

Palavras-chave: perfil mineral; espectroscopia atômica; espectroscopia vibracional; modelos de classe única.

ABSTRACT

Table salt, composed primarily of sodium chloride (NaCl), is widely used as a seasoning and preservative around the world. The most common types include refined salt, sea salt, Himalayan pink salt, fleur de sel, and light salt. Since its mineral composition varies according to geographic origin, it becomes possible to identify its provenance. This study aimed to authenticate the origin of table salt from four countries using flame atomic absorption spectroscopy (FAAS) and portable near-infrared (NIR) spectroscopy. Chemometric tools were applied to process the data, aiming to reduce dimensionality and facilitate interpretation. Principal Component Analysis (PCA) was used to decompose the original matrix, while the DD-SIMCA method (Data-Driven Soft Independent Modeling by Class Analogy) defined acceptance limits in the new space based on sample distances. The FAAS results revealed high variability in metal content among the countries. Brazilian salt showed higher Na content, while French salt stood out for its elevated levels of K, Zn, Fe, Mg, and Ca. When applying the DD-SIMCA models, Brazilian salt was completely separated from the others, with only five classification errors, confirming that the metal profile can serve as a fingerprint to identify salt origin. In the NIR spectral analysis, origin-related effects were primarily observed in the regions of 1300–1600 nm (second overtone of water) and below 1000 nm (third overtone). DD-SIMCA models using the first derivative of the NIR spectra resulted in 19 classification errors for raw salt, 23 for dried salt, and only 3 for dried and milled salt. These results indicate that particle size and moisture influence the spectra, highlighting bands attributed to free water and hydration water; after drying, correlations improved for Mg, Mn, and Cu contents. Finally, the performance of DD-SIMCA models based on spectra from dried and milled samples was similar to that obtained with FAAS data. Therefore, both FAAS and NIR techniques proved effective in identifying salt origin, with NIR representing a faster and lower-cost alternative, yielding results comparable to those of FAAS.

Keywords: mineral profile; atomic spectroscopy; vibrational spectroscopy; one-class models.

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1 INTRODUÇÃO

O sal de mesa, composto principalmente de cloreto de sódio (NaCl), é amplamente utilizado como tempero e conservante em todo o mundo. Diferentes tipos de sal de mesa incluem sal refinado, sal marinho, rosa ou sal do Himalaia, flor de sal e sal light (DA-COL *et al.*, 2015; GALVIS-SÁNCHEZ *et al.*, 2011; KUHN *et al.*, 2020). A principal fonte de extração de sal inclui o ambiente marinho, lagos com alto teor de salinidade, depósitos de rochas salinas e poços de sal (ZHANG *et al.*, 2020). A produção de sal é um processo que envolve a evaporação natural da água do mar em salinas, onde a água salgada é periodicamente introduzida, a qual evapora pelo calor e o sal cristaliza ao longo do tempo (SIDDIQUE *et al.*, 2023).

Entre os tipos mais consumidos, o sal refinado constitui a principal fonte de sódio na alimentação. Este tipo de sal passa por um processo de refinamento no qual a maioria dos nutrientes originais é perdida, restando apenas sódio e cloro (BRASIL, 2016; DUGGAL *et al.*, 2015). Em contraste, o sal marinho, obtido diretamente do mar, não é submetido a processos de refinamento tão extensos, mantendo uma quantidade superior de minerais, mas com valores de sódio semelhantes ao refinado (BRASIL, 2016; BASTOS *et al.*, 2017). O sal light, por sua vez, é composto por cerca de 50% de cloreto de sódio e 50% de cloreto de potássio, resultando em um teor de sódio significativamente menor (BRASIL, 2016). O sal do Himalaia, conhecido como sal rosa, é extraído de minas localizadas na região do Himalaia, e tem se tornado popular não apenas pelo uso na gastronomia, mas também pelas supostas propriedades minerais, incluindo oligoelementos como Cr, Fe e Zn (KUHN *et al.*, 2020), o que permite essa cor é a presença em sua composição de óxido de ferro (BASTOS *et al.*, 2017).

Segundo a Organização Mundial da Saúde (OMS), a ingestão média global de sódio por adultos é de 4.310 mg/dia (equivalente a 10,78 g/dia de sal), cerca do dobro do valor recomendado de ≤ 5 g/dia (2.000 mg/dia de sódio) (WHO 2025). O sal de cozinha é composto, em média, por 39,4% de sódio (Na) e 60,6% de cloreto (Cl) (WONG, 2018). O consumo excessivo de sódio é considerado o principal fator de risco dietético para as doenças crônicas não transmissíveis (MENTE *et al.*, 2018).

A composição mineral dos sais varia conforme a origem geográfica e o processo de produção. Por exemplo, a adição de iodo ao sal como iodeto de potássio (KI) ou iodato de potássio (KIO₃) para combater a deficiência nutricional desse elemento na dieta humana (GALIGA, SEVILLA, 2021). Outros compostos como

sulfatos, carbonatos e cloretos de magnésio e cálcio também podem estar presentes, dependendo do modo de processamento (DA-COL *et al.*, 2015; GALVIS-SÁNCHEZ *et al.*, 2011). O sal do Atlântico e do Mediterrâneo têm composições diferentes em relação ao cálcio, magnésio e potássio. Assim, a composição elementar do sal pode ser usada como uma impressão digital para identificar a sua origem (GALVIS-SÁNCHEZ *et al.*, 2011).

A espectroscopia atômica é uma metodologia consolidada para análise elementar (SOYLAK, MURAT, 2012), mas exige preparo demorado das amostras, profissionais especializados e instrumentação de alto custo. Como alternativas, métodos de fluorescência de raios X (DA-COL *et al.*, 2015) e espectroscopia no infravermelho próximo (NIR) (GALVIS-SÁNCHEZ *et al.*, 2011; GOWEN *et al.*, 2015) já foram aplicadas para análise de sal.

A espectroscopia NIR se apresenta como uma alternativa de natureza rápida e não destrutiva, e tem ganhado ampla aceitação e aplicação. É uma técnica molecular, que observa os padrões de reflexão e absorção de luz (radiação eletromagnética) na faixa do infravermelho próximo, que abrange comprimentos de onda de 780 a 2500 nanômetros (MALEGORI *et al.*, 2017, MABOOD *et al.*, 2017, CAPUANO *et al.*, 2014). Mediante o uso desta tecnologia, a amostra de interesse é exposta à luz e, em seguida, a luz refletida, conhecida como retroespalhamento, é quantificada por meio de um espectrômetro. Em comparação com outros métodos, este apresenta notável capacidade de penetração mais profunda, além de exigir menor rigor na preparação das amostras (PASQUINI, 2018, ESCÁRATE *et al.*, 2022).

Apesar das vantagens, a espectroscopia NIR gera sinais complexos que exigem a aplicação de métodos quimiométricos para interpretação (BONA *et al.*, 2018). Modelos baseados em análise discriminante são comumente utilizados para autenticação (GALVAN *et al.*, 2022), embora alguns autores argumentam que a análise discriminante é inadequada e que a melhor abordagem são os classificadores de classe única (OCC) (GRANATO *et al.*, 2018; RODIONOVA *et al.*, 2016). Esses métodos distinguem objetos de uma determinada classe de todas as outras classes (ZONTOV *et al.*, 2017). O modelo DD-SIMCA é baseado em PCA e na estimativa de métricas de distância e seus níveis de corte (POMERANTSEV, RODIONOVA, 2014), sendo uma das ferramentas mais simples e eficazes para essa finalidade (ZONTOV *et al.*, 2017).

A impressão digital química com análise multivariada de dados se tornou uma das abordagens sistemáticas mais poderosas para determinar a autenticidade. Ela

fornece um perfil característico da amostra baseado em sua qualidade ou origem (ESTEKI *et al.*, 2017).

Diante da variedade de sais no mercado, conhecer sua composição química auxilia o consumidor na tomada de decisão. Diante do exposto, este trabalho visa autenticar a origem de sal de mesa de quatro países utilizando espectroscopia de absorção atômica em chama e infravermelho próximo com equipamento portátil. A integração dessas técnicas com ferramentas quimiométricas permite uma análise mais robusta da composição e variabilidade geográfica dos sais.

Os resultados obtidos nesse trabalho foram publicados no periódico *Chemosensors* 2025, 13, 231, (Zanela Lima, L.R. *et al.*, 2025).

2 OBJETIVOS

2.1 Objetivo geral

Autenticar a origem de sal de mesa de quatro países utilizando espectroscopia de absorção atômica em chama e infravermelho próximo com equipamento portátil.

2.2 Objetivos específicos

- Coletar amostras de diferentes tipos de sal, incluindo sal refinado, sal marinho e flor de sal, oriundas do Brasil, França, Espanha e Portugal.
- Preparar as amostras por meio de secagem e moagem padronizadas, com o intuito de reduzir variabilidades analíticas.
- Obter espectros das amostras por espectroscopia no infravermelho próximo (NIR).
- Obter os dados elementares das amostras utilizando espectrometria de absorção atômica em chama, para determinação de potássio, sódio, cálcio, magnésio, ferro, manganês, zinco e cobre.
- Aplicar técnicas de quimiometria aos dados obtidos, com foco em análise exploratória e modelagem estatística multivariada.
- Desenvolver modelos estatísticos capazes de autenticar a origem geográfica das amostras de sal com base nas características químicas e espectrais.
- Comparar os resultados obtidos pelas diferentes técnicas, considerando o desempenho dos modelos estatísticos e a reprodutibilidade dos dados.

3 REVISÃO BIBLIOGRÁFICA

3.1 Sal de cozinha

A indústria do sal é uma das mais antigas e amplamente distribuídas globalmente sendo uma parte essencial na dieta para humanos e animais. O sal comum raramente é encontrado puro na natureza, pois frequentemente contém impurezas de componentes principais, como K^+ , Mg^{2+} , Ca^{2+} , CO_3^{2-} , SO_4^{2-} , água, matéria orgânica e minerais de argila e metais pesados, como Cd, Co, Cu, Fe, Mn, Ni, Pb e Zn. Suas concentrações variam de acordo com a composição da solução e com as características físico-químicas do sistema de evaporação (GAD, ABD EL BAKEY e SAKR, 2020).

O sal desempenha função fundamental na dieta e na indústria alimentícia por sua composição de cloreto de sódio, atuando como aditivo e conservante, melhorando textura, cor, sabor e vida útil dos produtos (CHOI *et al.*, 2014; YOTSUYANAGI *et al.*, 2018). Contudo, o consumo excessivo de sódio está associado a fatores de risco de doenças, causando danos à saúde humana (HU *et al.*, 2022). Sendo a principal causa do aumento da pressão arterial elevada, incidência de doenças cardiovasculares, entre outras (CHIU, VENKATAKRISHNAN, WANG, 2020). Já o cloro (cloreto) auxilia no transporte do dióxido de carbono das células e na absorção de potássio, sendo regulado pelos rins e pela transpiração (SILVA *et al.*, 2019).

3.1.1 Composição

A composição mineral do sal varia segundo a técnica de colheita, refinamento e o ambiente marinho (DUGGAL *et al.*, 2015). O sal refinado é composto principalmente de cloreto de sódio (39,4% de Na e 60,6% de Cl), perdendo a maioria dos nutrientes durante o refino (WONG, 2018). Já o sal não refinado, como o sal marinho ou sal-gema, mantém impurezas naturais, incluindo K, Mg e Ca, cujas concentrações variam com a salinidade da água e o método de extração (GALVIS-SÁNCHEZ *et al.*, 2011; LEE *et al.*, 2016).

O sal marinho, menos processado, apresenta teores minerais superiores, ainda que com quantidades de sódio semelhantes ao refinado. O sal light, mistura de 50% de cloreto de sódio com 50% de cloreto de potássio, possui teor reduzido de sódio (BRASIL, 2016). O sal rosa do Himalaia, extraído no Paquistão, destaca-se pela coloração (transparente, branca, rosa ou avermelhada) e presença de elementos como Fe, Ca e Mg. Essa coloração se deve à presença de óxido de ferro (BASTOS *et*

al., 2017; NAKASATO, 2004).

A composição química dos sais reflete sua origem e processo de extração. No sal marinho, os teores de K, Mg e Ca variam conforme a densidade da água salgada utilizada. Salinas abertas ao ambiente podem conter partículas do solo, elevando os níveis de Al, Ti, Si e Fe. Já os sais de rocha podem apresentar variações decorrentes de interações com água doce subterrânea ou reações químicas no subsolo (*LEE et al.*, 2016). Esses perfis minerais servem como “impressões digitais” que revelam a origem geográfica e os métodos de produção (*DI SALVO et al.*, 2023; *DANEZIS; GEORGIU*, 2022).

3.1.2 Sal iodado

A iodação do sal é uma estratégia global para prevenir distúrbios causados pela deficiência de iodo. Entre 1942 e 2020, 123 países adotaram legislação obrigatória de iodação; em 2021, esse número subiu para 126, com outros 21 permitindo a fortificação voluntária (*INTERCÂMBIO GLOBAL DE DADOS SOBRE FORTIFICAÇÃO*, 2021). A obrigatoriedade é vista como mais eficaz, embora a fortificação voluntária também possa garantir ingestão adequada de iodo.

No Brasil, a iodação do sal é obrigatória conforme a Resolução RDC 604/2022, aplicando-se ao sal refinado, moído e granulado (*BRASIL*, 2022). Em contrapartida, Portugal, França e Espanha permitem a iodação voluntária, com regulamentações orientativas, mas sem exigência legal (*INTERCÂMBIO GLOBAL DE DADOS SOBRE FORTIFICAÇÃO*, 2021).

3.1.3 Métodos de extração e tipos de sal

Na produção tradicional, o sal passa pelas etapas de preparo das salinas, evaporação e colheita (*MENDES et al.*, 2012). Inicialmente, a água do mar é limpa e concentrada por evaporação solar. Em cristalizadores, a salmoura atinge o ponto de saturação e precipita sal a uma taxa de 2,5 a 3 cm por mês. Ao atingir 15 a 18 cm de cristais, inicia-se a colheita, precedida por tratamento com produtos como ácido sulfúrico ou cloro. Após colhido, o sal é lavado, centrifugado e moído (*VALENTIM*, 2019).

O tipo de processamento influencia o produto final. O sal refinado é submetido a intensa purificação, no qual a maior parte dos nutrientes presentes se perde, restando basicamente sódio e cloro (*BRASIL*, 2016; *DUGGAL et al.*, 2015). O sal

grosso tem cristalização mais lenta e controle granulométrico menos rigoroso (RAMOS, 2018). O sal marinho e o sal rosa não passam por processos de refinamento tão extensos (BRASIL, 2016; BASTOS *et al.*, 2017).

A flor de sal, tipo especial valorizado em países como França e Portugal, é colhida manualmente nos primeiros cristais formados na superfície da salina, durante poucos meses do ano, sob condições específicas de sol e vento. Essa extração preserva o contato com microrganismos da salmoura, conferindo características únicas ao produto (DONADIO *et al.*, 2011).

3.2 Espectrometria de Absorção Atômica em Chama (FAAS)

A Espectrometria de Absorção Atômica em Chama (FAAS) é um método que apresenta elevada seletividade e sensibilidade, atingindo concentrações na ordem de ppm (partes por milhão) dos analitos em questão (GALIOTTO *et al.*, 2020). Além disso, essa técnica é amplamente reconhecida por sua precisão em medições de oligoelementos em diversas amostras. Segundo a Comissão Codex Alimentarius, as técnicas mais utilizadas, como a espectrofotometria de absorção atômica de chama (FAAS), a espectroscopia de emissão óptica com plasma indutivamente acoplado (ICP-OES) e a espectrometria de massa com plasma indutivamente acoplado (ICP-MS), são fundamentais para a determinação de oligoelementos (GONZÁLVEZ, ARMENTA, DE LA GUARDIA, 2015).

A composição elementar obtida por fornece informações que não são acessíveis por técnicas voltadas à fração orgânica (BAQUETA *et al.*, 2023). Estudos demonstram sua aplicabilidade, Gad, Abd El Bakey e Sakr (2020) determinaram as concentrações de chumbo, cádmio, cobalto e manganês em sais de quatro comunidades produtoras de sal (Ada, Nyanyano, Saltpond e Elmina) e de duas marcas de sais refinados em Gana. Essas concentrações foram medidas utilizando espectrometria de absorção atômica.

De forma semelhante, outro estudo encontrou metais traço, como cobre, níquel, cobalto, manganês, chumbo e cádmio, em 28 amostras de sal de cozinha refinado e não refinado provenientes da Turquia, Egito e Grécia. Esses metais foram determinados por espectrometria de absorção atômica de chama (SOYLAK, PEKER, TURKOGLU, 2008).

Adicionalmente, metodologias para análise do teor de Fe, Mn, Mg e Ca em xaropes de cana usando FAAS combinado com outras técnicas foram desenvolvidas e validadas. Os resultados da análise multivariada mostraram que os íons metálicos

podem ser usados como indicadores de origem geográfica ou contaminação durante a fabricação ou processamento, ajudando, assim, a garantir a qualidade alimentar e a segurança desse adoçante (ALVES, ANDRADE, FELSNER, 2023).

No entanto, é importante considerar que, durante a análise de traços de íons de metais pesados com FAAS, os efeitos de interferência de matrizes complexas podem impedir a análise direta. Os baixos níveis de detecção nas amostras analisadas podem ser superiores ao limite de detecção do instrumento FAAS usado. Por isso, torna-se necessário desenvolver técnicas de separação e enriquecimento com elevada precisão e sensibilidade antes da análise com FAAS (SOYLAK, ALASAAD, ÖZALP, 2022).

3.3 Espectroscopia de Infravermelho Próximo (NIR)

A espectroscopia de infravermelho próximo (NIR) é uma técnica vibracional que se baseia na absorção de radiação eletromagnética na faixa de 780 a 2500 nm. Esta técnica oferece informações relacionadas às vibrações moleculares de ligações químicas dos componentes estruturais primários das moléculas, como as ligações simples C-H, N-H, S-H e O-H (MEDEIROS *et al.*, 2022).

O NIR é um método instrumental que fornece uma grande quantidade de dados que devem ser processados adequadamente para fornecer informações práticas. Assim, o uso da quimiometria é essencial para o tratamento das informações contidas nos espectros NIR (AHMAD *et al.*, 2016; BONA *et al.*, 2018). Essas técnicas fornecem uma breve descrição de conjuntos de dados multivariados, de modo que a análise de espectro total pode ser considerada (RANZAN *et al.*, 2014). A espectroscopia de infravermelho associada à quimiometria é uma técnica não destrutiva e rápida em pesquisas ambientais e alimentares (BONA *et al.*, 2017; PEREIRA *et al.*, 2018; SHI E YU, 2017; VIEIRA *et al.*, 2019).

Devido à necessidade de preparação mínima ou nenhuma da amostra, a espectroscopia NIR apresenta vantagens como sendo simples, rápida, não invasiva, econômica e ecologicamente correta pois não envolve uso de produtos químicos (MILLATINA *et al.*, 2024).

3.4 Quimiometria

A quimiometria envolve a aplicação de métodos estatísticos e matemáticos para interpretar e organizar grandes volumes de dados obtidos em análises

químicas, auxiliando na sua compreensão e aplicação prática (GALVAN *et al.*, 2023). Essa abordagem permite a extração de informações relevantes, a identificação de padrões e características de interesse, além da redução da dimensionalidade de dados e assim facilitando a interpretação dos resultados (ANDRADE, COELHO, UARROTA, 2020; FARRES *et al.*, 2019).

Dentre os ramos que compõem essa área, destacam-se o planejamento experimental, a identificação de padrões e os modelos de calibração multivariada. Essa última abordagem visa desenvolver modelos que relacionem medições, como espectros ou concentrações químicas, com características específicas das amostras analisadas (SOUZA; POPPI, 2012).

Nesse contexto, destaca-se a importância da quimiometria na análise de dados produzidos por espectrofotômetro, especialmente na região do infravermelho, cujos espectros tendem a ser complexos e de difícil interpretação (FARRES *et al.*, 2019). Devido à presença de ruído de fundo e bandas sobrepostas, é necessário aplicar o uso de análises multivariadas ou métodos quimiométricos que possibilitem o desenvolvimento de modelos apropriados para elucidar as relações entre os espectros e os parâmetros de qualidade ou composição selecionados (ACHATA, 2018).

Dessa forma, a quimiometria é amplamente utilizada em três etapas principais: o pré-processamento de dados, a construção de modelos de classificação ou regressão e, por fim, a validação desses modelos (MOGHADDAM *et al.*, 2022).

3.4.1 Pré Processamento

O pré-processamento, é uma etapa essencial e frequentemente a primeira a ser realizada na análise quimiométrica de dados espectrais. Essa etapa tem como principal objetivo reconhecer, corrigir ou eliminar interferências que podem comprometer a interpretação correta dos espectros (MOUSA *et al.*, 2021; GALVAN *et al.*, 2023).

Os espectros obtidos, especialmente em técnicas como a espectroscopia no infravermelho próximo (NIR), podem conter ruídos indesejáveis resultantes de variações instrumentais, condições ambientais não controladas, espalhamento de luz, flutuações na linha de base e interferências aleatórias. O pré-processamento atua justamente para diminuir esses efeitos e permitir que os modelos

quimiométricos construídos sejam mais robustos e confiáveis (MOUSA *et al.*, 2021; RODRIGUEZ-SAONA *et al.*, 2016).

3.4.2 Análise de Componentes Principais (PCA)

A Análise de Componentes Principais (PCA) é utilizada como ferramenta exploratória multivariada para identificar padrões, tendências e possíveis agrupamentos nos dados espectrais. Adicionalmente, métodos de seleção de variáveis são aplicados para remover informações redundantes e destacar as regiões espectrais mais relevantes para a modelagem. (MEDEIROS *et al.*, 2022). É uma técnica não supervisionada de análise multivariada que reduz as dimensões espectrais em componentes principais (PC), as quais capturam a máxima variabilidade dos dados e preservam as informações espectrais significativas (XU *et al.*, 2018).

A partir desses PC's, a primeira componente principal (PC1) explica a máxima variância presente no conjunto de dados, enquanto a segunda (PC2) explica o máximo variância restante, sendo ortogonal à ela e não tem nenhuma correlação com a PC1 (GRANATO *et al.*, 2018). Assim, as seguintes PC's são ortogonais às anteriores, representando a máxima variância (KUMAR, SHARMA, 2018).

3.4.3 Modelagem Independente por Analogia de Classe (SIMCA)

O SIMCA é um método de reconhecimento de padrões baseados na similaridade, com isso, cada categoria de interesse é modelada individualmente e então os objetos são aceitos ou rejeitados por cada modelo de classe. Como os limites das regiões são definidos independentemente uns dos outros, pode acontecer que uma amostra seja aceita por mais de uma classe ou rejeitada por qualquer uma delas (FIRMANI, 2019). Para todas as versões do SIMCA, são considerados dois parâmetros estatísticos: as distâncias de escores (SD) e as distâncias ortogonais (OD). A definição das áreas de decisão para objetos regulares, extremos e *outliers* é baseada nessas distâncias estatísticas (KARIMVAND *et al.*, 2024).

O DD-SIMCA é uma modificação do método SIMCA, que apenas diferencia no cálculo do limite de aceitação que limitam a classe autêntica. Este método é utilizado para problemas de autenticação de classe única (*one class*) utilizado como uma ferramenta de reconhecimento padrão, sendo apenas a classe alvo modelada.

A classe alvo é construída de acordo com as propriedades da amostra, e essas propriedades podem ser sinais analíticos gerados por equipamentos, como espectroscopia (RODIONOVA *et al.*, 2016).

Na primeira etapa, O DD-SIMCA aplica a análise por componentes principais (PCA) nos dados de treinamento da classe alvo, este de PC's determina a complexidade do modelo e tem um impacto significativo na qualidade da classificação. Quanto maior for o número de PC's, maior será a parte da variação dos dados de treinamento explicada pela decomposição de PCA. Ao mesmo tempo, a inclusão de componentes desnecessários pode resultar em um modelo que não considera apenas as características principais da classe, mas também o ruído indispensável. Sendo assim, para selecionar a complexidade do modelo, o princípio da parcimônia é regularmente aplicado (RODIONOVA *et al.*, 2016; CIZA *et al.*, 2019).

4 MATERIAL E MÉTODOS, RESULTADOS E DISCUSSÃO

Estas sessões estão apresentadas em formato de artigo científico, segundo resolução interna do Ppgta CM/MD.

Artigo submetido à revista *International Chemosensors* 2025, 13, 231.

5 ORIGIN IDENTIFICATION OF TABLE SALT USING FLAME ATOMIC ABSORPTION AND PORTABLE NEAR-INFRARED SPECTROMETRIES

Abstract

The mineral composition of table salt can be indicative of its origin. This work evaluated the possibility of identifying the origin of salt from four countries: Brazil, Spain, France, and Portugal. Eight metals were quantified through flame atomic absorption/emission spectroscopy (FAAS). The possibility of using portable near-infrared spectroscopy (NIR) as a faster and lower-cost alternative for identifying salt provenance was also evaluated. The content of Ca, Mg, Fe, Mn, and Cu was identified as possible markers to differentiate the salt origin. One-class classifiers using FAAS data and DD-SIMCA could discriminate the salt origin with few misclassifications. For NIR spectroscopy, it was possible to highlight the importance of controlling the humidity and granulometry before the spectra acquisition. After drying and milling the samples, it was possible to discriminate between samples based on the interaction between the water of hydration and the presence of the cations in the sample. The Mg, Mn, and Cu are important in identifying the origin of salt using NIR spectra. The DD-SIMCA model using NIR spectra could classify the origin with the same performance as observed in FAAS. However, it is important to emphasize that NIR spectroscopy requires less sample preparation, is faster, and has low-cost instrumentation.

Keywords: mineral profile; atomic spectroscopy; vibrational spectroscopy; one-class modeling; data-driven soft independent modeling by class analogy.

Introduction

Table salt, mainly composed of sodium chloride (NaCl), is widely used as a seasoning and preservative worldwide. Different table salt types are available: refined salt, sea salt, pink or Himalayan salt, flower salt, and light salt [1–3]. Iodine is sometimes added to the salt as potassium iodide (KI) or potassium iodate (KIO₃) to decrease the deficiency in the human diet [4]. Depending on the manufacturing process, other

compounds were also found, like magnesium and calcium sulfates, carbonates, and chlorides [2,3]. The geo-graphic origin of the salt also influences its the salt mineral profile; for example, Atlantic and Mediterranean salt have different compositions regarding calcium, magnesium, and potassium [3]. The mineral profile can give different properties to table salt, adding value to the product, so it is important to guarantee traceability. Recent fraud scandals and food safety incidents have increased interest in food traceability. Food fraud leads to economic losses and the deterioration of the consumer's trust, and it can also threaten human health. Therefore, more consumers want more detailed information about their foods, such as the geographical origin, species, and transport and storage conditions [5]. Considering these facts, the elemental composition of the table salt could be used as a fingerprint to identify the salt's origin.

Atomic spectroscopy is a consolidated methodology for elemental analysis [6]. Although this method requires time-consuming sample preparation, it demands expert analysts and high-cost instrumentation. Therefore, alternatives such as X-ray fluorescence [2] and near-infrared spectroscopy (NIR) [3,7] were already applied for salt analysis. NIR spectroscopy, which requires few sample preparation steps, is commonly applied in food authenticity and origin identification [8–10]. Furthermore, low-cost portable spectrometers are available for NIR spectroscopy, allowing this analysis to be applied to different foods [11,12]. NIR is a vibrational spectroscopy, but some authors demonstrate that metals could be indirectly identified and quantified due to the changes in the shape and peak position of the water peaks in the NIR spectrum. The extent of these changes depends upon properties such as size and ionic strength, and this effect is also known as aquaphotomics [7,13,14]. The aquaphotomic effect allows the NIR spectra to quantify analytes in very low concentrations [14]. Despite the advantages already mentioned, NIR spectroscopy generates complex signals that require the application of chemometric methods to interpret the results [15]. Models based on discriminant analysis are the typical approach for dealing with authentication problems [16]. However, some authors argued that discriminant analysis is inappropriate and that the best approach is one-class classifiers (OCC) [17,18]. These methods distinguish objects of one particular class from all other classes [19]. The data-driven soft independent modeling by class analogy (DD-SIMCA) consists of a PCA model and an estimation of the orthogonal and score distances and their cut-off levels [20].

This work aimed to identify the origin of table salt from four countries by applying

flame atomic absorption and near-infrared spectroscopies. The data collected by these two spectroscopies generated DD-SIMCA models to distinguish the table salt from different countries. The objective is to verify whether NIR spectra are sufficient to produce models to identify table salt's origin. Therefore, this is the first work that applies NIR spectra in tan-dem with DD-SIMCA to classify the origin of table salt.

2. Materials and Methods

2.1. Samples

Fifty-nine salt samples bought in local markets were analyzed: 11 from Brazil (Figure S1—Supplementary Materials), 16 from Spain (Figure S2), 16 from France (Figure S3), and 16 from Portugal (Figure S4). The samples had different colors, humidity levels, and granulometry. Different types of salt were analyzed (label information), including flower salt, refined salt with or without iodine, sea salt, and light salt (sodium chloride was partially substituted by potassium chloride; SB1, SB2, SB3, and SF11). Therefore, the sample set has many different characteristics, and it was chosen to assess whether it is possible to identify the country of origin, even with these variations.

2.2. Humidity Analysis

The humidity was determined by weighing 10 g of the sample into a previously tared porcelain capsule. Heated for 3 h in an oven at 105 °C, cooled in a desiccator to room temperature, and weighed again. This procedure was repeated until a constant weight was achieved [21].

2.3. Flame Atomic Absorption/Emission Spectrometry Analysis

Potassium, sodium, calcium, magnesium, iron, manganese, zinc, and copper content in the salt samples was carried out in a flame atomic absorption spectrophotometer equipped with hollow cathode lamps (Perkin Elmer, model PinAAcle 900T, Waltham, MA, USA). For each element, the parameters and experimental conditions employed (wave-length, bandwidth, electric current, and gas flow rates) were set as recommended by the manufacturer.

About 0.05 g of salt was dissolved in 50 mL of HNO₃ (2%) to determine K, Na, and Ca. Nearby, 0.50 g of salt was dissolved in 25 mL of HNO₃ (2%) to determine Fe,

Mn, Cu, Mg, and Zn. CsCl was added to the sample to determine K and Na, guaranteeing a final concentration of 1.0 g L^{-1} . LaCl_3 (1.0 g L^{-1}) was added to the sample before determining Ca and Mg.

All standard solutions for the calibration curves were prepared from commercial solutions (1000 ppm) of different metals (Panreac, Darmstadt, Germany) diluted with HNO_3 (5%). The concentration range of the calibration curves was 0.25 to 5.00 ppm for K, Ca, and Fe; 0.13 to 2.50 ppm for Na; 0.12 to 1.25 ppm for Mg; 0.12 to 4.00 ppm for Mn; 0.13 to 2.00 ppm for Cu; and 0.05 to 1.00 ppm for Zn. When necessary, samples were diluted to bring the concentration closer to the center of the calibration curve.

2.4. Near-Infrared Spectrometry Analysis

All spectra were obtained in the DLP NIRscan Nano evaluation module (Texas Instruments, Dallas, TX, USA). The DLP NIRscan Nano GUI was used to control the spectrometer and collect the spectra in reflectance mode. The scan configuration used was the Hadamard method, with a range of 900–1600 nm, a width of 4.68 nm, a digital resolution of 530 points, and an exposure time of 0.635 ms, resulting in a total scan time of ~17 s. The salt samples were put in polyethylene bags and analyzed in three different forms to evaluate the influence of granulometry and humidity in the spectra: (i) raw salt; (ii) dried salt (the samples were kept in an oven at $105 \text{ }^\circ\text{C}$ for 24 h); and (iii) dried-milled salt (after dried, the salt was milled in tube-mill (IKA, Staufen, Germany) at 10000 rpm for 1 min and then sieved using a 100 mesh nylon cloth). The spectra acquisition was repeated three times for each sample; the plastic bags containing the sample were shaken between acquisitions. After the acquisition, the spectra were transferred to MATLAB R2024b (MathWorks, Natick, MA, USA), smoothed with a cubic smoothing spline (smoothing parameter 0.005). The first derivative was determined using the central finite-difference method (CFDM). The objective of the first derivative is to eliminate the shift in the baseline, which is common in reflectance spectra obtained from powdered samples. For the data analysis step, the mean spectra were used.

2.5. Data Analysis

A one-way ANOVA was applied to assess whether there were significant differences between the mean results of the metal profile. In cases with $p\text{-value} < 0.05$, Tukey's test checked the equality of means of two independent samples. When

comparing medians, Wilcoxon's rank sum test, a nonparametric test, was used. Samples with significant differences (p-value < 0.05) were represented with different letters.

The metals' data were determined using FAAS, and the first derivative of the NIR spectra was used for unsupervised exploration using principal component analysis (PCA). For the PCA, all wavelengths of the first derivative of NIR spectra were considered (900–1600 nm, resolution ~2 nm), and the matrix was mean-centered before analysis. The salt classification was performed using DD-SIMCA with a rigorous approach to defining the number of PCS, chi-square acceptance area, classic method, and $\alpha = 0.05$. The FAAS data were mean-centered and scaled, and the first derivative of the NIR spectra was mean-centered before DD-SIMCA modeling. We recommend reading the specialized literature for more information about the DD-SIMCA parameters [22]. All data analysis was made in MATLAB R2024b, and for DD-SIMCA, a graphical user interface (GUI) was used [19].

3. Results and Discussion

3.1. Humidity

The humidity for each sample is presented in the Supplementary Material (Table S1). Figure 1 shows the box plot to resume humidity variation in the samples for each country. Brazilian salt (SB) and Spain salt (SE) had less variation in humidity than France's salt (SF) and Portugal's salt (SP). The median is 0.1444% for SB, 0.1790% for SE, 0.3938% for SF, and 0.3343% for SP. SE had one sample with abnormally high humidity, and SP had three with higher humidity. These three SP samples were flower salt.

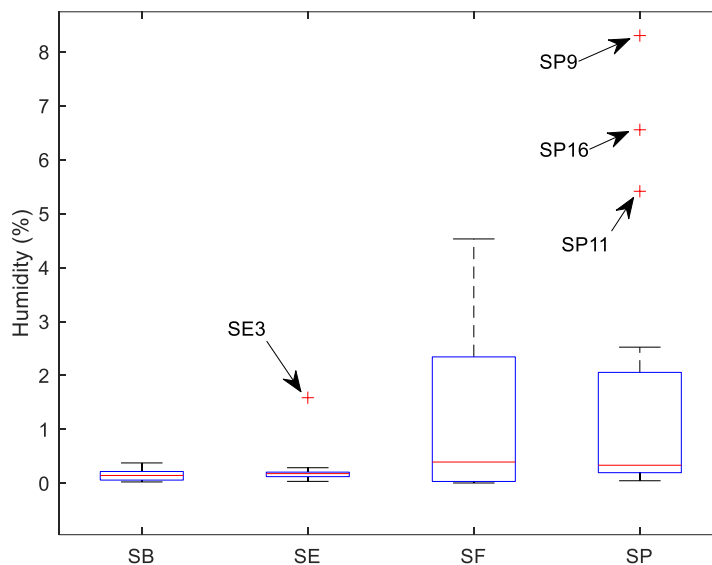


Figure 1. Box plot for humidity variation according to each country.

3.2. Flame Atomic Absorption/Emission Spectrometry

The table with eight metals quantified for each sample with FAAS is shown in the Supplementary Material (Table S2). Table 1 presents some descriptive statistics for each metal and country. The high variability for metal content for all countries stands out, as seen in the standard deviation values, variation range, and the difference between the mean and median. Only for potassium and sodium, statistically significant differences ($p > 0.05$) were not observed between the means of the countries. The sample SF11 (light salt) had an exceptionally high potassium content (about 81 times higher than the SB2, the second sample with the highest potassium content). The potassium concentration determined by FAAS to SF11 followed the potassium content declared in the salt package. The values obtained for the metal profile followed other consulted works [1–3].

Table 1. Descriptive statistics for metals quantified using FAAS.

Country	Minimum	Maximum	Median *	Mean **	Standard Deviation
K ($\mu\text{g g}^{-1}$)					
SB	169	4.22×10^3	251 ^a	1.21×10^3 ^a	1.66×10^3
SE	126	1.23×10^3	356 ^a	379 ^a	242
SF	36.9	3.42×10^5	770 ^a	2.20×10^4 ^a	8.54×10^4

SP	65.0	4.03×10^3	296 ^a	711 ^a	1.04×10^3
Na (mg g ⁻¹)					
SB	341	648	421 ^{ab}	451 ^a	94.7
SE	382	557	418 ^b	441 ^a	51.3
SF	134	601	400 ^a	398 ^a	89.9
SP	177	606	415 ^{ab}	404 ^a	121
Ca (µg g ⁻¹)					
SB	347	1.05×10^3	540 ^b	593 ^b	203
SE	97.2	1.08×10^3	610 ^b	569 ^b	274
SF	113	1.81×10^3	355 ^b	692 ^b	596
SP	0.622	1.23×10^3	77.7 ^a	154 ^a	299
Mg (µg g ⁻¹)					
SB	77.9	635	132 ^a	236 ^a	174
SE	35.2	1.45×10^3	867 ^b	719 ^a	530
SF	21.8	7.28×10^3	1.61×10^3 ^{ab}	2.20×10^3 ^b	2.37×10^3
SP	4.17	6.06×10^3	580 ^b	1.16×10^3 ^{ab}	1.56×10^3
Fe (µg g ⁻¹)					
SB	0.286	53.3	1.80 ^b	7.09 ^{ab}	15.4
SE	0.027	2.34	0.127 ^a	0.579 ^a	0.854
SF	0.0187	105	0.869 ^{abc}	19.5 ^b	31.6
SP	1.70	8.79	5.09 ^c	5.17 ^{ab}	2.01
Mn (µg g ⁻¹)					
SB	0.111	1.11	0.545 ^a	0.616 ^a	0.327
SE	0.0126	2.69	1.86 ^b	1.42 ^a	1.00
SF	0.0111	6.55	1.16 ^{ab}	1.89 ^a	1.95
SP	1.52	7.08	3.81 ^c	4.08 ^b	1.58
Zn (µg g ⁻¹)					
SB	0.103	0.270	0.192 ^a	0.193 ^a	0.0480
SE	0.00893	0.601	0.229 ^a	0.267 ^a	0.152
SF	0.208	1.20	0.562 ^b	0.602 ^b	0.227
SP	0.0790	0.853	0.506 ^b	0.471 ^b	0.242
Cu (µg g ⁻¹)					
SB	0.357	1.93	0.445 ^{bc}	0.737 ^{bc}	0.564
SE	0.0663	0.425	0.196 ^a	0.186 ^a	0.0941
SF	0.125	0.775	0.444 ^b	0.445 ^{ab}	0.136
SP	0.266	1.54	0.942 ^c	0.948 ^c	0.383

* Median values with different letters are statistically different (p -value < 0.05) in Wilcoxon's rank sum test. ** Mean values with different letters are statistically different (p -value < 0.05) in Tukey's test.

In Figure 2, the radar plot highlights each country's metal profile differences. The radar plot indicates that SP generally has a higher content of Cu and Mn and a lower content of Ca than other countries. SF has a higher content of Mg, Fe, and K. However, it is important to highlight the abnormal content of K in sample SF11 (Table S2, Supplementary Material), which raises the mean for France's salt. Therefore, these differences must be carefully evaluated due to the high variation in the content of metals within samples from the same country.

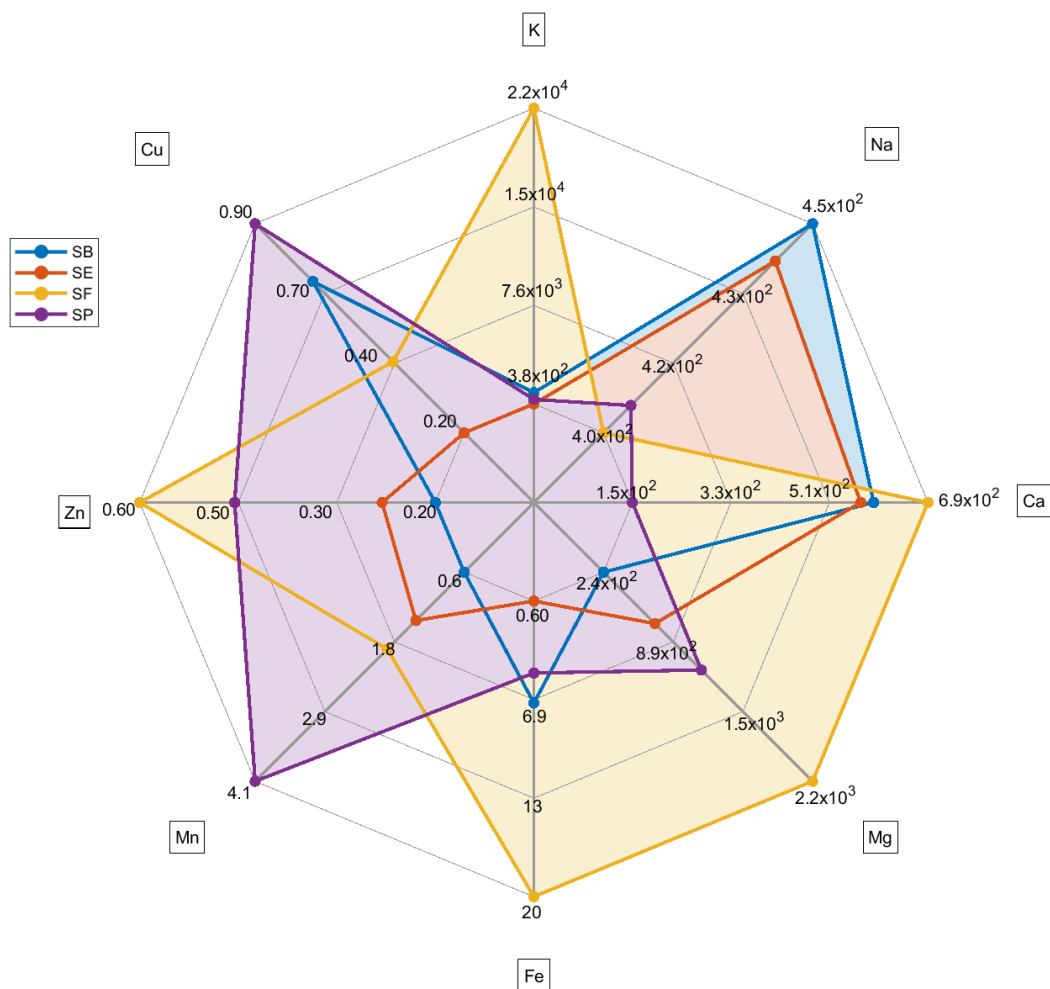
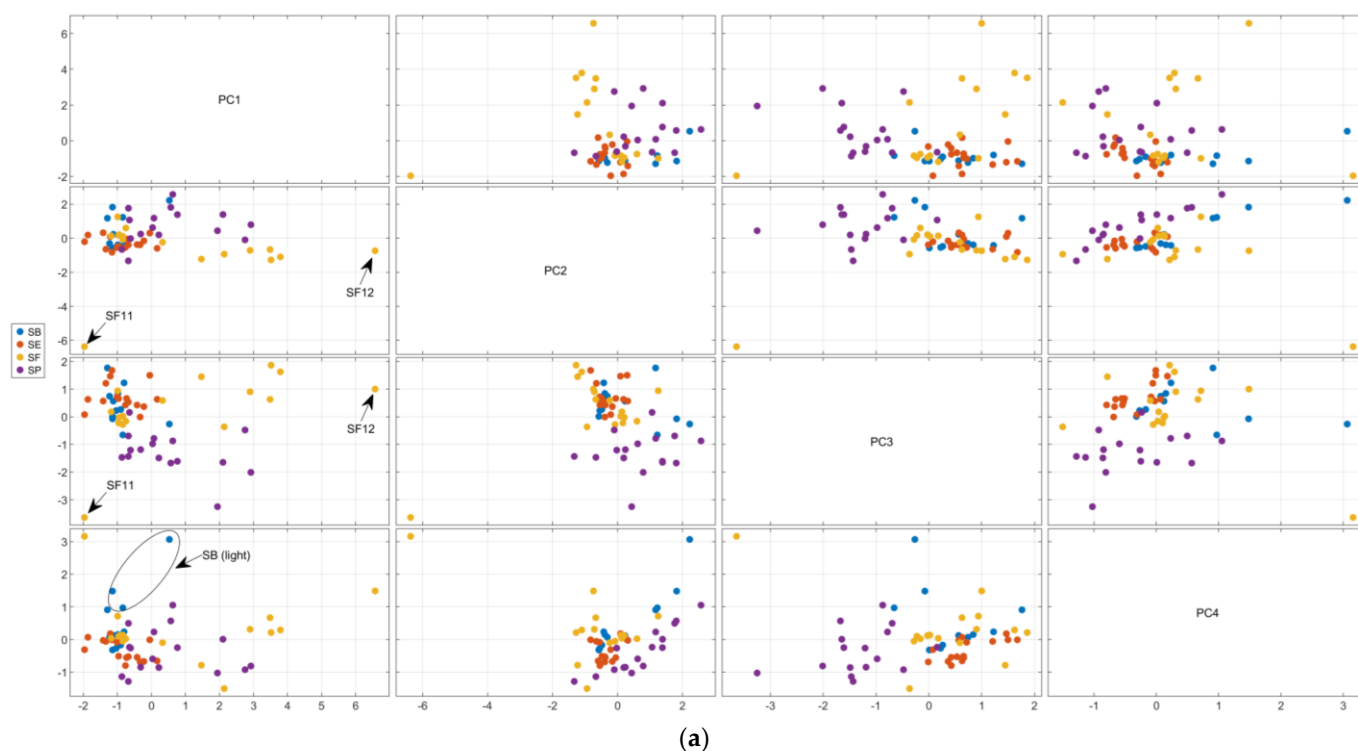


Figure 2. Radar plot for each mean metal content (mean values) based on the country of the salt. For sodium concentration, the unit is mg g^{-1} . For the other metals, the concentration unit is $\mu\text{g g}^{-1}$.

The autoscaled matrix of the metal content in salt samples was submitted to the PCA. The scree and Pareto plots show that the first four principal components (PC) contributed most to representing the mineral content data (Supplementary Material—Figure S5). Furthermore, according to Figure S5c, PC5 has some information about Mg and PC6 about Zn. Nevertheless, looking at the scores plot for these PCs, there is no relevant separation for the samples, so they were not considered in the analysis. The first four PCs accumulated 79.3% of the total variance, with 34.9% in PC1, 18.6% in PC2, 16.8% in PC3, and 9.0% in PC4. Figure 3 resumes the PCA results obtained for metal content. All samples SE (except SE9) and SB (except SB2) had negative scores for PC1 (Figure 3a). The loadings (Figure 3b) indicate the highest positive weights for Zn, Fe, Mg, and Mn. So, the SE and SB samples have the lowest average contents for

these salts, except for iron in the SB samples (see radar plot—Figure 2). In PC2, almost all SP samples had positive scores, while SB, SE and SF had negative scores. The positive loading (Figure 3c) for the Cu content (highest mean value for SP) and K content (highest mean value for SF) was the main factor for this separation. In PC3, the SP samples had negative scores due to the lowest calcium content compared to other countries. The PC4 represents the difference in potassium content, and the light salt samples had positive scores. In Figure 3, it is possible to observe that some samples separated from the other salts. SF11, as mentioned before, had the highest level of potassium. SF12 had the highest level of magnesium. The light salt from Brazil was separated from other samples from this country due to its potassium content.



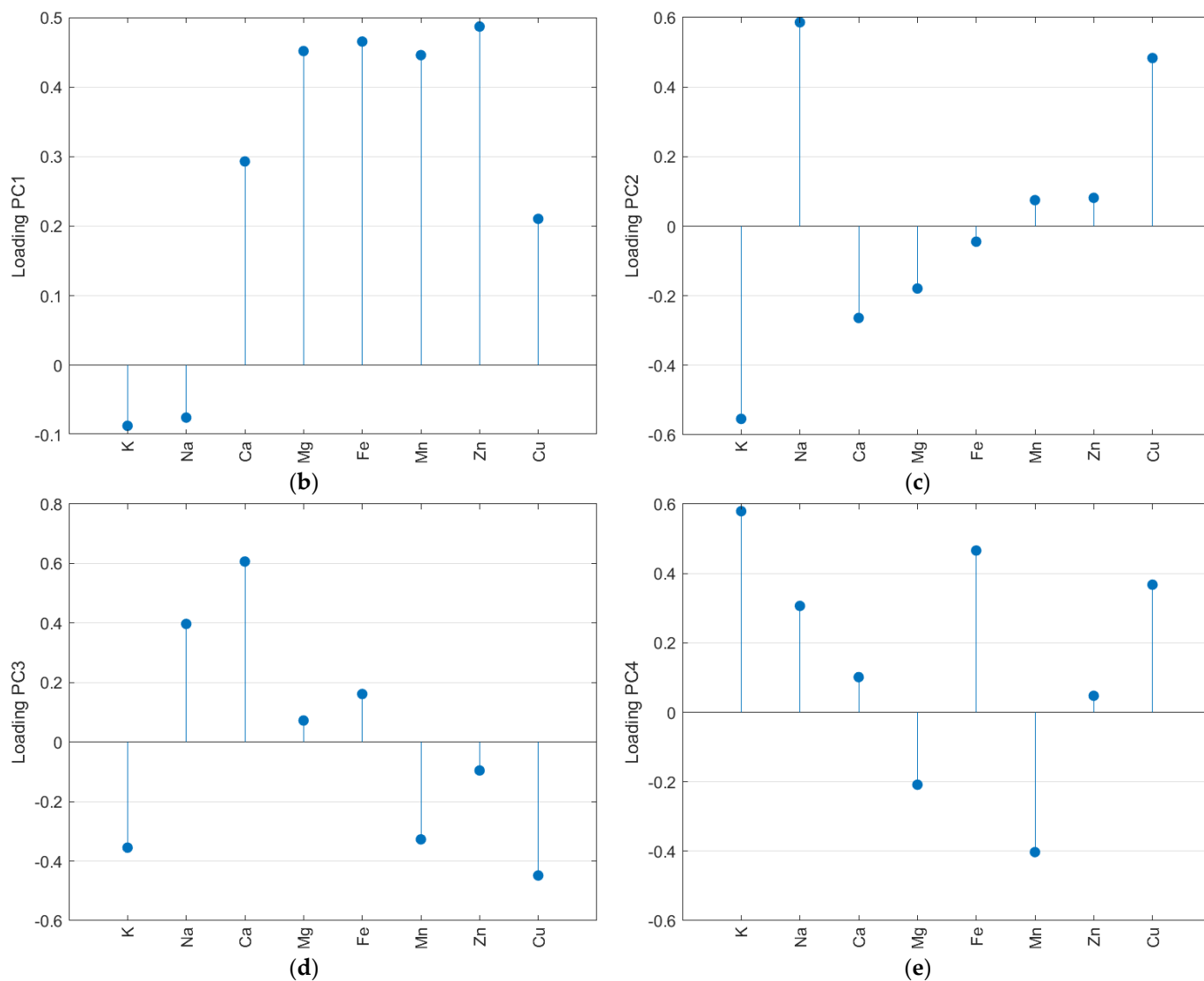
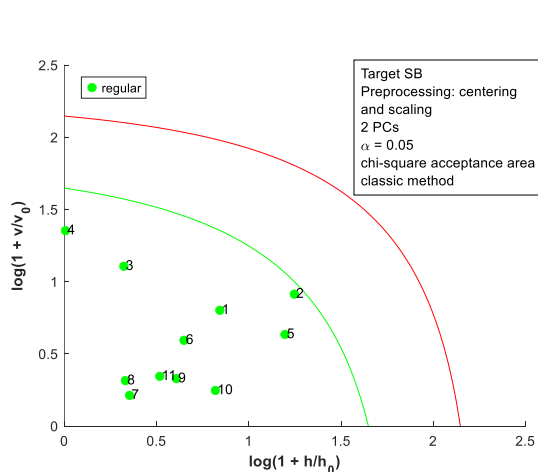


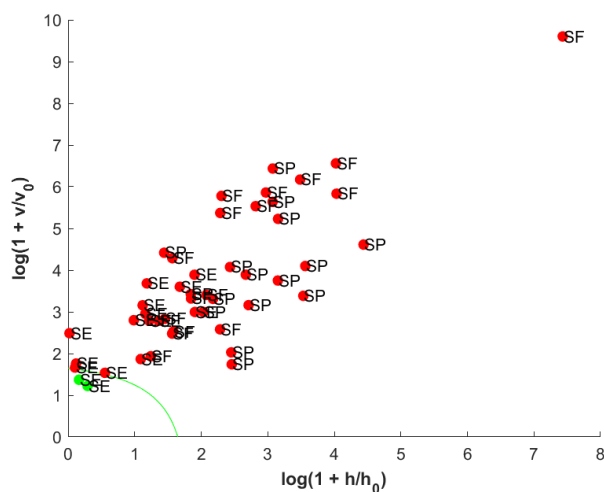
Figure 3. Principal component analysis of the autoscaled mineral content matrix: score plot for the first four PCs (a), loadings for PC1 (b), PC2 (c), PC3 (d), and PC4 (e).

The DD-SIMCA [19] was employed to build OCC models for the metal content matrix, and the acceptance plots for each country are presented in Figure 4. In the acceptance plot, each sample is plotted using the score distance (h) and the orthogonal distance (v). The values h_0 and v_0 are scaling factors found during the model calibration step [22]. The autoscaled matrix was used for all OCC models due to the difference in the scale observed for the metal content matrix. In each model, the smallest number of PCs was used to allow adequate separation of the samples. For SB salt (Figure 4a,b), two samples of SE were misclassified (100% sensitive and 95.8% specific). For SE, one false negative was observed, and two samples of SB were misclassified (93.8%

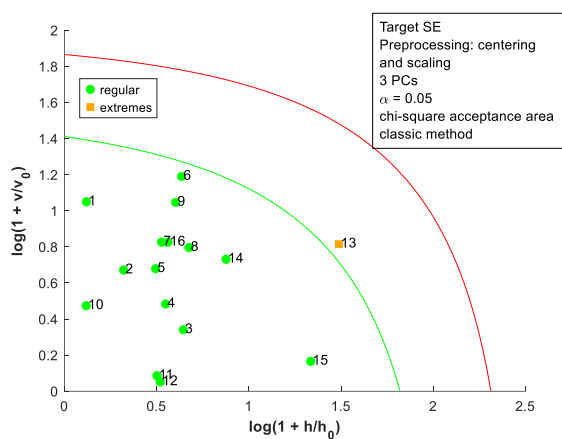
sensitive and 95.3% specific); for SF, two samples of SB were misclassified (100% sensitive and 95.3% specific); and for SP, one sample of SE was misclassified (100% sensitive and 97.8% specific). Considering the samples' variability, the OCC models achieved good performance (seven false positives and one false negative). Therefore, the metal content could be used as a fingerprint to identify the country of origin for salt samples.



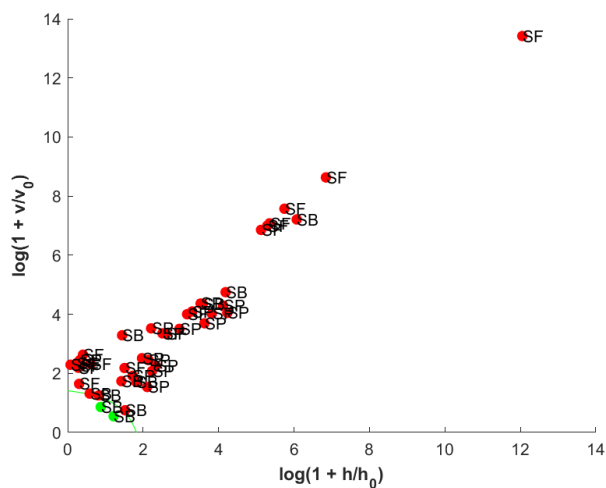
(a)



(b)



(c)



(d)

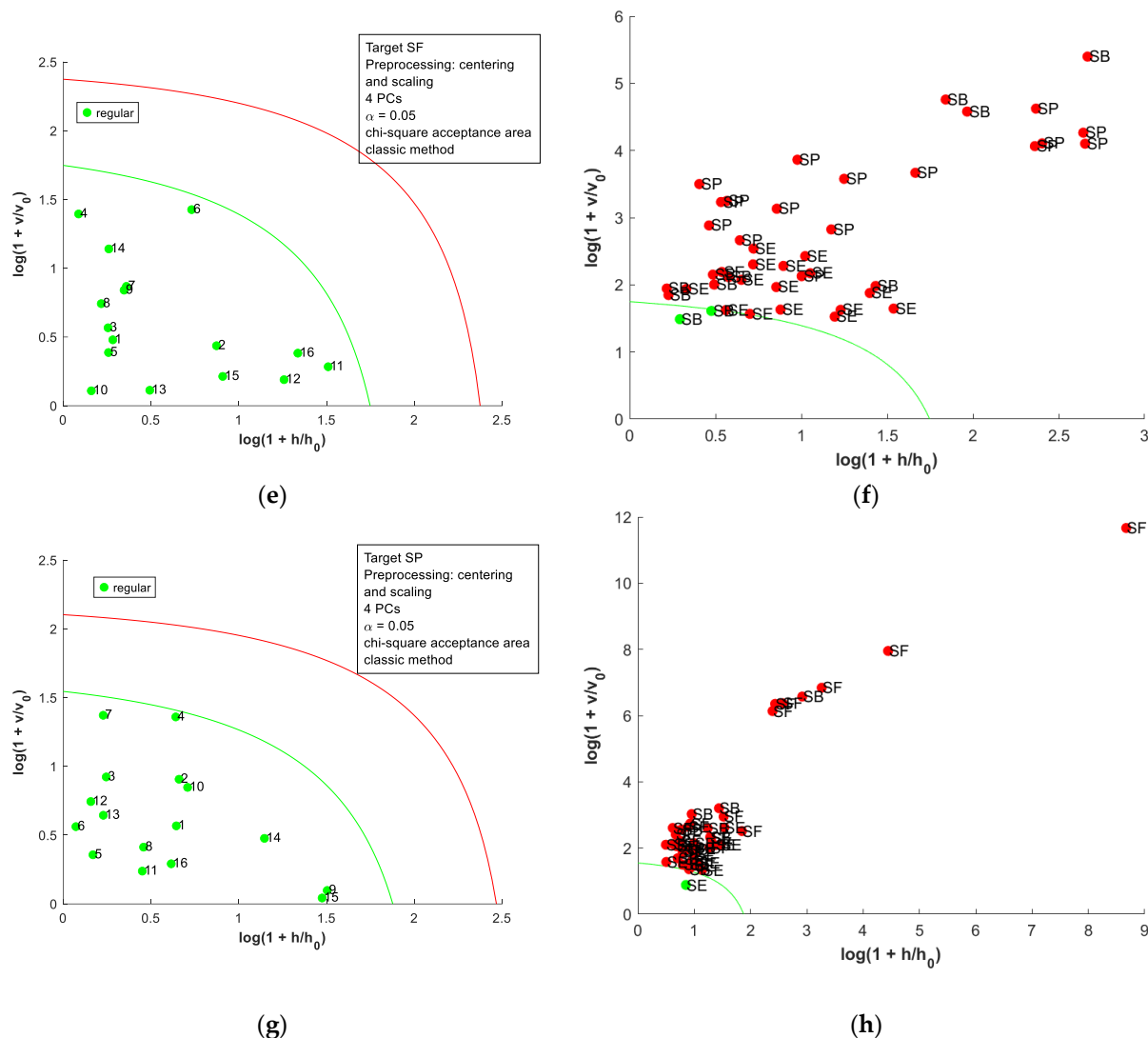


Figure 4. Acceptance plots for DD-SIMCA using the metal content table: (a) target class SB; (b) test class SE, SF, and SP; (c) target class SE; (d) test class SB, SF, and SP; (e) target class SF; (f) test class SB, SE, and SP; (g) target class SP; and (h) test class SB, SE, and SF. The green line is the acceptance border, and the red line is the outlier border.

3.3. Near-Infrared Spectrometry

Figure 5a shows the effect of the sample preparation on the NIR spectra. Water content and particle-size distribution are two factors that directly influence the NIR spectrum [14]. Therefore, the effect of these two factors on the table salt classification is first discussed. The major differences occur in the 1300–1600 nm region, which contains the second overtone for water. It is possible to observe minor changes in the third overtone water region below 1000 nm. The effect of the salt origin on the spectra could be observed for raw, dried, and dried-milled salt, as presented in Figure 3b–d.

The spectra profile is similar to other works [2,7].

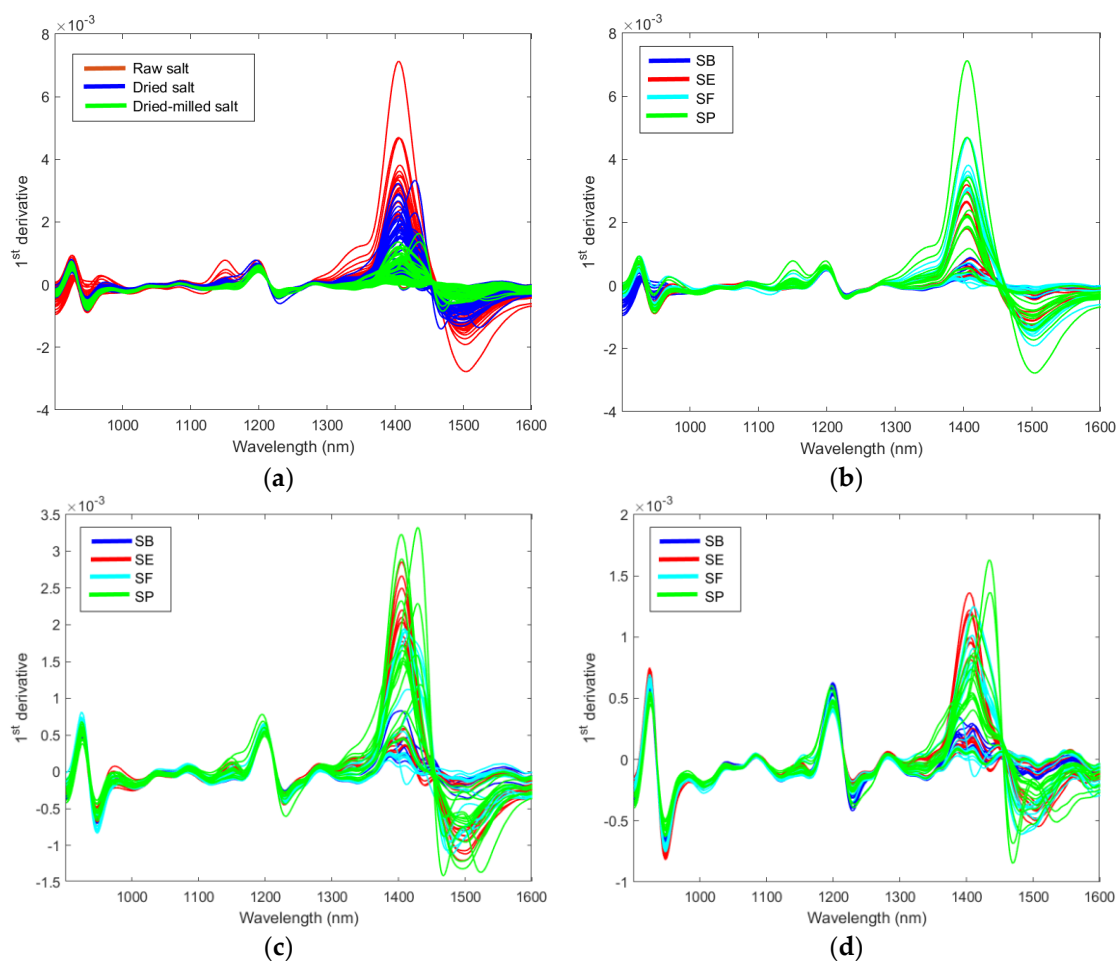


Figure 5. The first derivative of the NIR spectra: effect of the salt preparation in the spectra (a); effect of the country of origin in the spectra of raw salt (b), dried salt (c), and dried-milled salt (d).

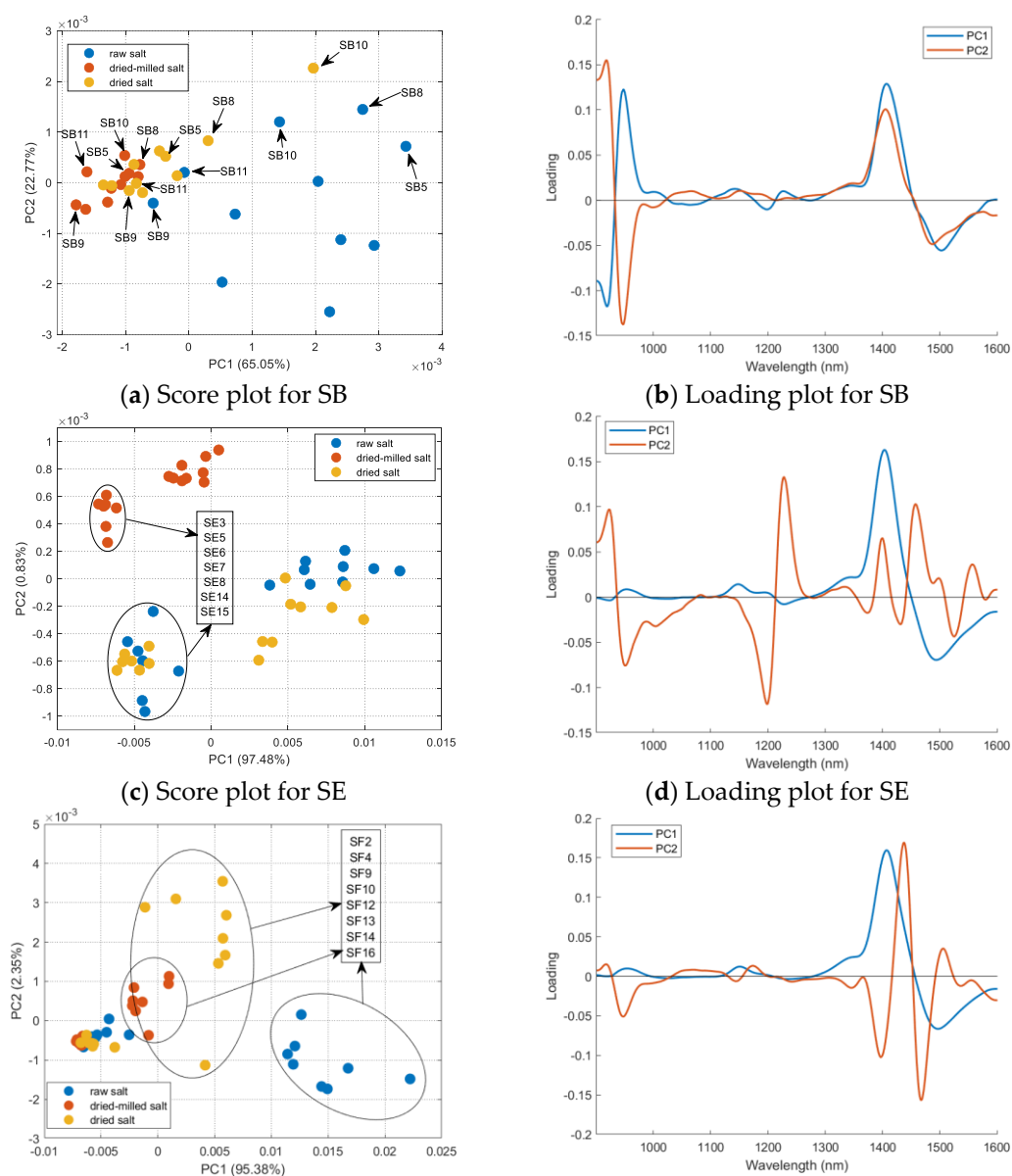
A PCA (mean center matrix) of the sample's spectra obtained for each country was performed to better understand the effect of sample treatment, and the results are summarized in Figure 6. For Brazilian salt (Figure 6a), the raw salt samples had positive scores in PC1 (except SB9 and SB11); the dried and dried-milled samples had negative scores in PC1 (except SB10 and SB8 for dried salt). Sample SB11 presented the lowest humidity (0.0246%); however, sample SB5 had the highest humidity (0.3771%) considering the Brazilian salt. Samples SB8 and SB10 were coarse salt; only after milling were these samples grouped with other Brazilian samples. The loading plot (Figure 6b) shows that regions 1300–1600 nm and below 1000 nm had a major influence

on the separation observed in PC1. As mentioned before, these regions are related to the second and third water overtone, respectively. The distribution of the samples in the PC2 is maintained with the treatments applied to the salt samples. For example, SB9 always had negative scores in PC2, independent of the treatment used before NIR spectrum acquisition. On the other hand, SB10 or SP10 always had positive scores. For SF and SE, it is possible to see that samples were divided into two groups, which were the same regardless of the treatment used before NIR spectrum acquisition. Therefore, PC2 contains spectral information about the samples' composition independent of granulometry or humidity.

For Spain, the circled and boxed groups are the same samples listed but for different treatments of the table salt (Figure 6c). The dried-milled salt samples form a separate group, and raw and dried salt samples form another group. Furthermore, SE samples were split into two groups. This separation is maintained regardless of the treatment applied to the samples. Comparing these two groups' humidity and metal profiles (Table S3), it is possible to see a great difference between Mg and Mn. The separation between these two groups is mainly represented in PC1. The loading plots show that the 1350–1550 nm region has a higher weight for the distribution of the samples in PC1. Water can be associated with salts even after drying in an oven as saline hydrates. The water of hydration or crystallization refers to water found in the crystalline framework of a salt. The determination of salt by NIR is based on the behavior of the water component in the spectrum due to changes in hydrogen bonding, resulting in band shifts (aquaphotonic) [14]. When the salt-induced changes in the water spectrum can be isolated from other spectral variations, salt detection could be improved [23]. Thus, after eliminating humidity and granulometry standardization, the NIR spectra highlighted the absorption bands associated with water in saline hydrates. We acquired some spectra of magnesium chloride hexahydrate, manganese chloride tetrahydrate, sodium chloride, and mixtures to test this hypothesis (Figure S6). Before the spectra acquisition, the same procedure was used for salt preparation (drying and milling steps). These spectra confirmed that hydrate salts had bands in the 1300–1600 nm region. The spectra for SE12 (highest manganese content in SE samples) and SE13 (highest magnesium content in SE samples) were also plotted for comparison. Previous work also related these effects in near-infrared spectra [2].

Salt samples from France showed similar behavior to that observed for salt from

Spain, separating into two groups regardless of the treatment applied. The circled and boxed groups are the same samples listed, but for different treatments of the table salt (Figure 6e). Comparing the other evaluated properties (Table S3) for these two groups, we observed variability in humidity, which is eliminated after drying. The metal profile showed major differences for potassium, calcium, magnesium, iron, and manganese. Figure S6c shows the NIR spectra for calcium chloride dihydrate and iron (III) chloride hexahydrate with absorption bands in the 1300–1600 nm region. Potassium chloride does not have water of hydration, so its spectrum is similar to sodium chloride. The spectra for SF2 (highest calcium content in SF samples) and SF13 (highest iron content in SF samples) were also plotted to compare with the hydrate salts.



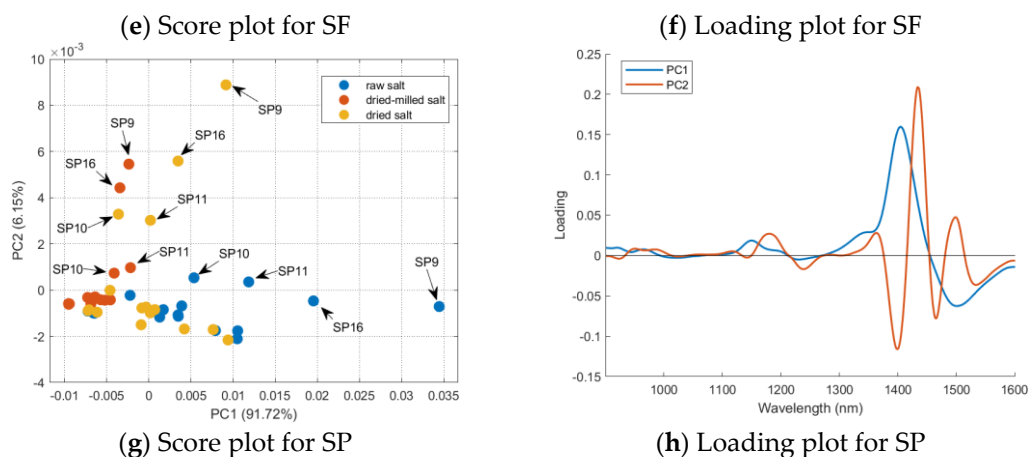
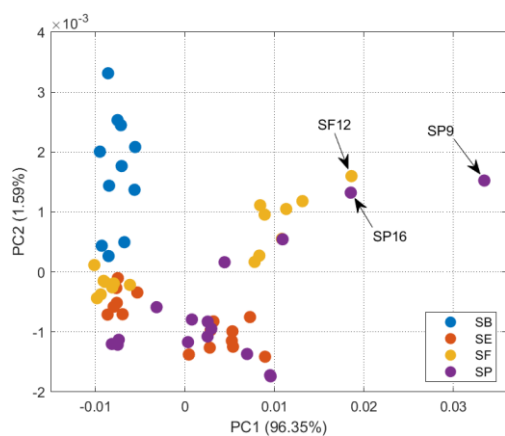


Figure 6. PCA for the mean-centered first derivative of the spectra for the raw, dried, and dried-milled samples of each country: (a) score plot and (b) loading plot for SB; (c) score plot and (d) loading plot for SE; (e) score plot and (f) loading plot for SF; and (g) score plot and (h) loading plot for SP.

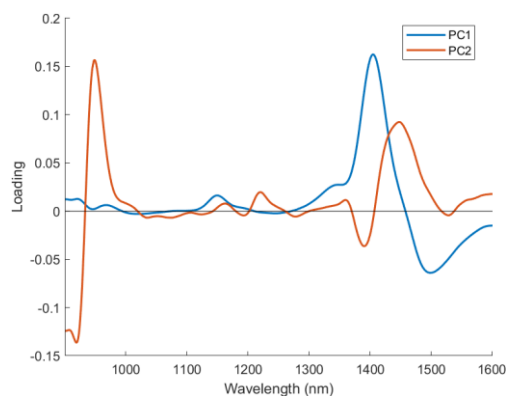
Samples SP9, SP10, SP11, and SP16 were separated from the others for Portugal. These four samples were flower salt, which had more humidity, potassium, calcium, and magnesium (Table S3). Once again, NIR spectra separated salt according to minerals that form hydrates, resulting in a shift in the water band at ~1400 nm.

Considering that the sample's treatment interferes with the analysis, a PCA for each salt treatment was performed to evaluate the effect of the countries in the salt spectra. For raw salt, it is possible to see in the loading plot (Figure 7b) that the samples' distribution in PC1 is due to the 1350–1550 nm region, which contains the second overtone for water. The samples SP9, SF12, and SP16, highlighted in Figure 7a, had a higher positive score in PC1 and humidity (Table S1). There is a correlation between PC1 scores and sample humidity ($r = 0.58$, $p\text{-value} = 1.43 \times 10^{-6}$). Figure S7 confirms that higher correlations between the spectra' first derivative and humidity occur in the 1350–1550 nm region. This correlation is not observed in PC2 ($r = 0.19$, $p\text{-value} = 0.15$). Otherwise, PC2 separates SB (positive scores) and SE (negative scores). The loading plot (Figure 7b) indicates the region below 1000 nm and between the range 1350 and 1500 nm, with a major contribution to this separation. Comparing the mean and median values for metal profile (Table 1) for SB and SE suggests that Fe, Cu, Mg, and Mn were the most important differences. However, PC2 scores (Figure 7a) did not present a higher correlation with the values for these metals ($r_{\text{Mg}} = 0.09$, $p_{\text{Mg}} = 0.48$, $r_{\text{Fe}} = 0.32$,

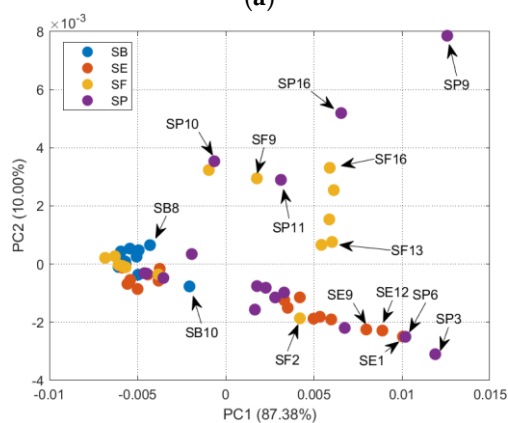
$p\text{Fe} = 0.01$, $r\text{Mn} = -0.22$, $p\text{Mn} = 0.10$, $r\text{Cu} = 0.38$, $p\text{Cu} = 3.00 \times 10^{-3}$). In the correlation plots between the raw salt spectra' first derivative and metal content (Figure S8), Mn content correlated with the regions below 1000 nm and 1350–1500 nm, Mg and Fe contents correlated only with the last region, and Cu did not have important correlations. The DD-SIMCA was applied to the first derivative of NIR spectra for raw salt (Figure S9 and Table S5). Four PCs were necessary for better results, but nineteen samples were misclassified. Only SB was successfully classified; for SE, two samples of SP were misclassified; for SF, four samples of SE, two samples of SP, and one sample of SB were misclassified; for SP, ten samples of SE were misclassified.



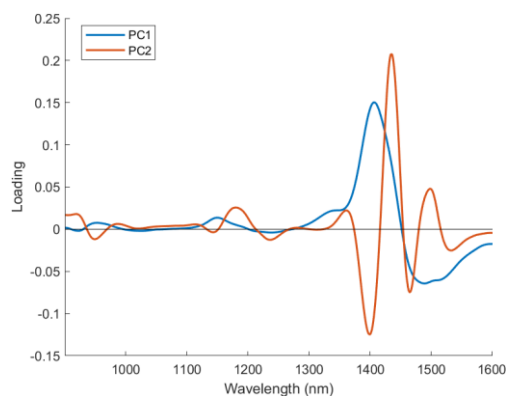
(a)



(b)



(c)



(d)

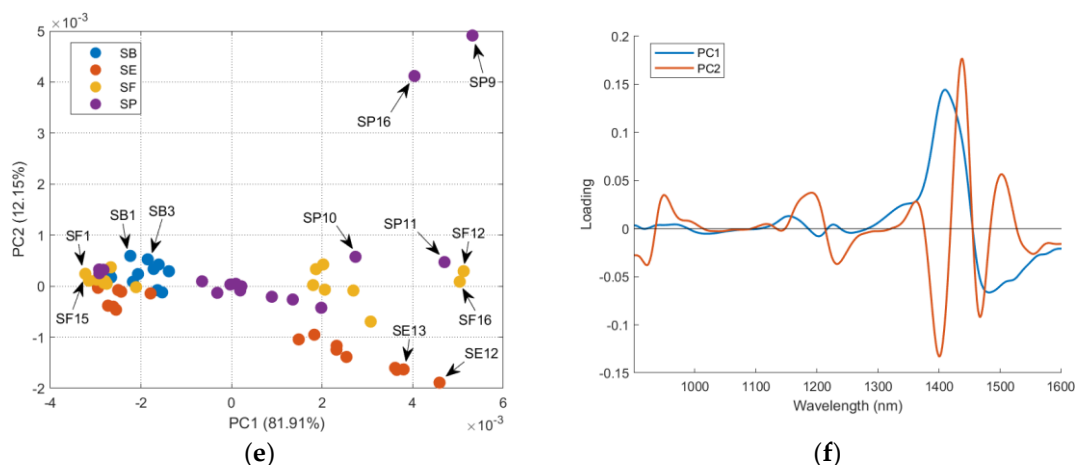


Figure 7. PCA of the mean-centered first derivative of the spectra of the four countries for each salt treatment: (a) score plot and (b) loading plot for raw salt; (c) score plot and (d) loading plot for dried salt; and (e) score plot and (f) loading plot for dried-milled salt.

For dried salt (Figure 7c), the distribution of the samples in PC1 and PC2 was related to the mineral content, as previously discussed. The granulometry differences may interfere with the distribution, but it is not easy to establish a relation between the grain size and PCA distribution. The DD-SIMCA using the dried salt spectra (Figure S10 and Table S5) performs the worst compared to other salt treatments and FAAS data, with twenty-three misclassifications. For SB, one sample of SE and one sample of SP were misclassified; for SE, one sample of SP and one sample of SB were misclassified; for SF, five samples of SE, one sample of SP, and one sample of SB were misclassified; for SP, six samples of SE and six samples of SB were misclassified.

For dried-milled salt (Figure 7e), it is possible to see (PC1) the same distribution in two groups for SE, SF, and SP, as previously in Figure 6. The SB samples remain grouped considering the PC1 and PC2 axes. Table 2 presents the correlations between the scores (PCA for dried-milled salt) and the metal content determined via FAAS.

Table 2. Correlations between PC1 and PC2 scores (dried-milled salt) and the metal content of the samples.

Metal	PC1	PC2
K	-0.1230	0.0572
Na	-0.1350	-0.0019
Ca	-0.3409 *	-0.0396
Mg	0.7503 *	0.2969 *
Fe	0.2214	0.0444
Mn	0.6573 *	0.2701 *
Zn	0.3896 *	0.2155
Cu	0.0582	0.4787 *

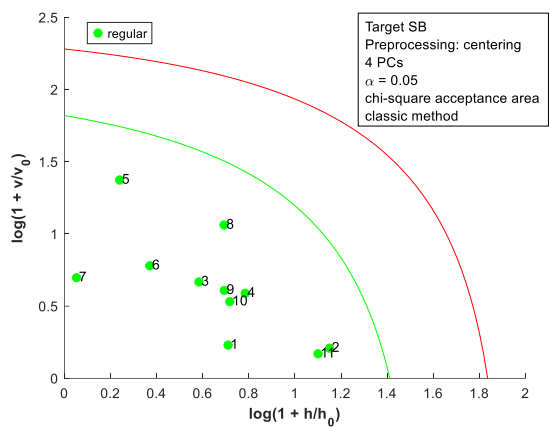
* Statistically significant correlations ($p < 0.05$).

The PC1 had significant correlations with Mg, Mn, and Cu; a negative correlation with Ca was observed. The samples with higher scores for PC1 (SP9, SF12, SF16, and others) also have higher values for Mg (Table S2). Otherwise, samples with lower scores for PC1 (for example, SF1 and SF15) have lower levels of Mg. The same behavior is presented for the other metals, with significant correlations with PC1, but it is less evident than the trend for Mg. The loadings for PC1 (Figure 6f) indicate that the 1300–1600 nm region had more weight for the observed distribution of the samples. As previously discussed, this region is related to the OH bond from the salts' water of hydration, the aquaphotonic effect [14]. The correlation plot between the dried-milled salt spectra' first derivative and metal contents (Figure S11) confirms that this region had higher correlations with Mg and Mn.

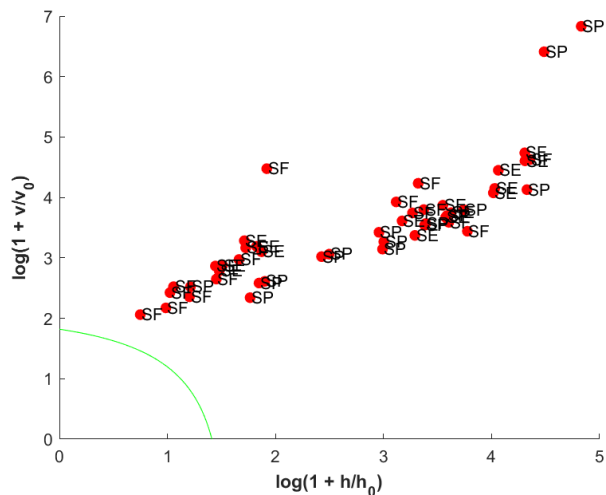
The PC2 mainly separates the SP9 and SP16 samples from the others. The correlations with PC2 scores indicate a relationship with Cu, Mg, and Mn. The loadings for PC2 have higher values for the region between 1350–1550 nm, near 1200 nm, and below 1000 nm. The first region correlates more with Mg and Mn, and the second and third regions correlate more with Cu (Figure S11).

The acceptance plots for the DD-SIMCA model using the first derivative of the driedmilled salt NIR spectra are presented in Figure 8. Only three misclassifications, false positives, were observed; two SE (SE7 and SE8, labeled as sea salt) and one SB (SB10, labeled refined salt) samples were classified as SF. Therefore, DD-SIMCA models reached 100% sensitivity and were 100% specific for SB, SE, and SP. For SF, the DD-SIMCA model was 100% sensitive and 93.0% specific. A comparison between all DD-SIMCA models was provided in Table S5 in the Supplementary Material. The classification performance for NIR spectra of the dried-milled salt was superior to that for FAAS data. Furthermore, the NIR has less sample preparation, cost, and time consumption than FAAS.

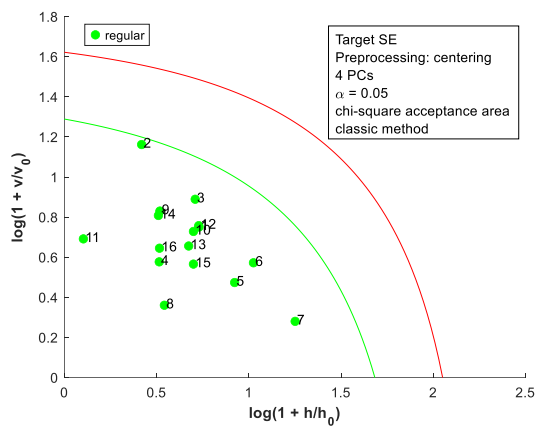
It is important to highlight that possible correlations between the elements quantified using FAAS and the NIR spectra were analyzed. However, other elements different from those quantified may also interfere with the water of hydration and, consequently, with the NIR spectrum of the sample. Thus, better classification performance was obtained with the NIR spectra because other unidentified elements may be contributing to differentiating the origin of the different table salts analyzed.



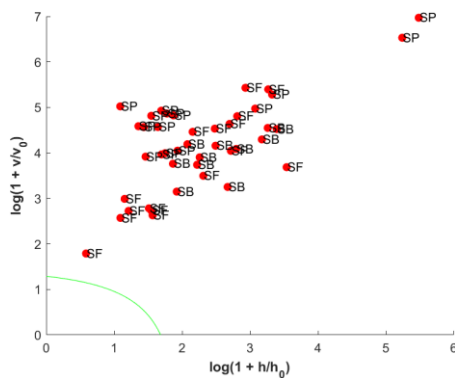
(a)



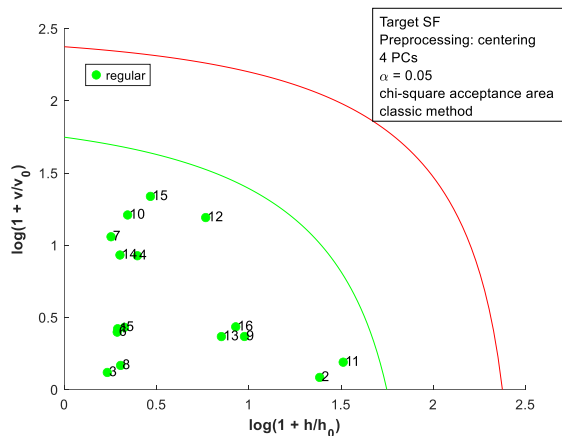
(b)



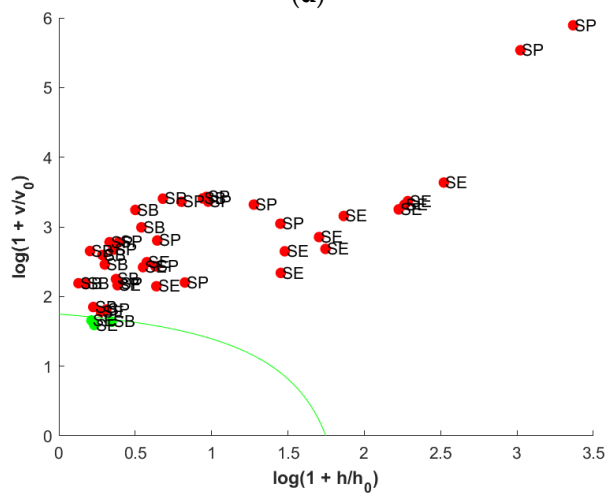
(c)



(d)



(e)



(f)

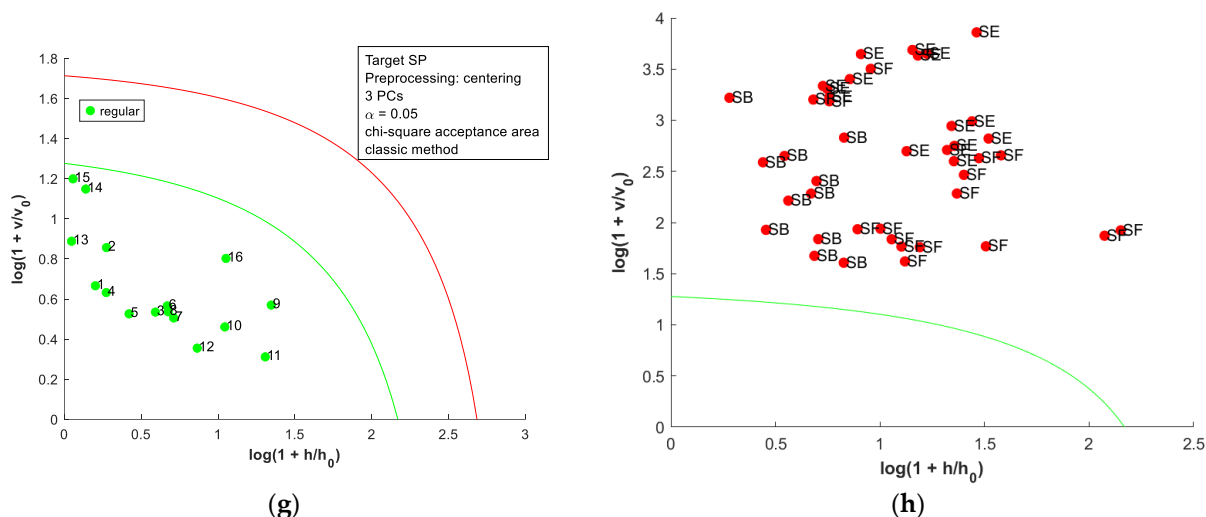


Figure 8. Acceptance plots for DD-SIMCA using the first derivative of NIR spectra from dried-milled salt of each country: (a) target class SB; (b) test class SE, SF, and SP; (c) target class SE; (d) test class SB, SF, and SP; (e) target class SF; (f) test class SB, SE, and SP; (g) target class SP; (h) test class SB, SE, and SF. The green line is the acceptance border, and the red line is the outlier border.

4. Conclusions

The FAAS spectroscopy showed differences between the mineral content of the salts from Brazil, Spain, France, and Portugal, with major differences for Ca, Mg, Fe, Mn, and Cu. A large variation in the amount of minerals was also observed for samples from the same country. The DD-SIMCA model, using the FAAS data, separated the salt according to the country of origin with few misclassifications.

The granulometry and humidity were important parameters that interfered with the NIR spectra. The NIR spectra presented absorption bands related to the humidity in the salt and with water of hydration from some salts. After drying, the NIR spectra for salt samples showed a higher correlation with Mg, Mn, and Cu contents. The DD-SIMCA model using the spectra for dried-milled samples had a similar performance (three misclassifications) compared to the FAAS data.

Both FAAS and NIR spectroscopy identified the origin of the salt samples, but NIR is a simpler and faster analysis that produces results equivalent to FAAS. Our results demonstrate a great variability in the composition of table salt from different countries. These data reinforce the importance of using accurate analytical methods, such as FAAS and alternative instruments, and portable NIR, to authenticate the origin or detect possible fraud in table salt. In future work, it will be important to analyze more samples, including more countries and products with fraud, and verify the possibility of

using other machine learning algorithms to interpret and model the data obtained.

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6 CONCLUSÃO

A espectrometria FAAS evidenciou diferenças no conteúdo mineral dos sais provenientes do Brasil, Espanha, França e Portugal, com destaque para as variações nos teores de Ca, Mg, Fe, Mn e Cu. Observou-se também grande variabilidade na concentração desses minerais entre amostras de um mesmo país. O modelo DD-SIMCA, aplicado aos dados de FAAS, conseguiu separar as amostras de sal conforme o país de origem, com poucos erros de classificação.

A granulometria e a umidade foram parâmetros relevantes que influenciaram os espectros NIR, os quais apresentaram bandas de absorção associadas à umidade presente no sal e à água de hidratação de alguns sais. Após a secagem, os espectros NIR mostraram maior correlação com os teores de Mg, Mn e Cu. O modelo DD-SIMCA, baseado nos espectros das amostras secas e moídas, apresentou desempenho semelhante ao modelo com dados de FAAS, com apenas três erros de classificação.

Tanto a espectrometria FAAS quanto NIR foram eficazes na identificação da origem das amostras de sal, no entanto, a NIR destaca-se por ser uma técnica mais simples, rápida e com resultados equivalentes aos da FAAS.

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APÊNDICE A – Material suplementar do artigo

Table S1. Humidity for salt samples (SB = Brazilian salt, SE = Spain salt, SF = France salt, and SP = Portugal salt).

SAMPLE	HUMIDITY (%)	SAMPLE	HUMIDITY (%)
SB1	0.0823 ± 0.0042	SF1	0.0050 ± 0.0070
SB2	0.2185 ± 0.0103	SF2	4.1835 ± 0.7399
SB3	0.1607 ± 0.0313	SF3	0.0497 ± 0.0282
SB4	0.0505 ± 0.0223	SF4	2.5300 ± 0.7975
SB5	0.3771 ± 0.0373	SF5	0.0530 ± 0.0447
SB6	0.2498 ± 0.0178	SF6	0.0265 ± 0.0250
SB7	0.1444 ± 0.0023	SF7	0.0365 ± 0.0208
SB8	0.2166 ± 0.0120	SF8	0.0547 ± 0.0071
SB9	0.0590 ± 0.0138	SF9	0.7329 ± 0.2397
SB10	0.0586 ± 0.0141	SF10	1.4967 ± 0.0355
SB11	0.0246 ± 0.0141	SF11	0.0298 ± 0.0001
SE1	0.2021 ± 0.0418	SF12	4.5315 ± 0.0644
SE2	0.2088 ± 0.0261	SF13	1.1787 ± 0.0570
SE3	1.5869 ± 0.4317	SF14	2.1581 ± 0.0583
SE4	0.1543 ± 0.0068	SF15	0.0265 ± 0.0208
SE5	0.0961 ± 0.0251	SF16	2.8611 ± 0.0177
SE6	0.1529 ± 0.0403	SP1	0.1596 ± 0.0532
SE7	0.0348 ± 0.0071	SP2	0.3827 ± 0.2424
SE8	0.0398 ± 0.0001	SP3	0.2365 ± 0.0513
SE9	0.2183 ± 0.0343	SP4	0.2996 ± 0.0350
SE10	0.2037 ± 0.0072	SP5	0.2327 ± 0.0720
SE11	0.1925 ± 0.0205	SP6	0.3657 ± 0.0363
SE12	0.1891 ± 0.0005	SP7	0.0766 ± 0.0353
SE13	0.2882 ± 0.0126	SP8	0.0466 ± 0.0306
SE14	0.0599 ± 0.0001	SP9	8.3035 ± 0.2897
SE15	0.1493 ± 0.0146	SP10	2.5242 ± 0.0343
SE16	0.1688 ± 0.0004	SP11	5.4154 ± 0.1707
		SP12	0.9728 ± 1.5990
		SP13	0.3028 ± 0.1144
		SP14	1.5884 ± 0.9461
		SP15	0.1598 ± 0.1776
		SP16	6.5564 ± 0.0674

Table S2. Metals quantified (dry basis) using flame atomic absorption spectrometry (FAAS).

Sample	K ($\mu\text{g g}^{-1}$)	Na (mg g^{-1})	Ca ($\mu\text{g g}^{-1}$)	Mg ($\mu\text{g g}^{-1}$)	Fe ($\mu\text{g g}^{-1}$)	Mn ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)	Cu ($\mu\text{g g}^{-1}$)
SB1	4195.75	550.28	422.65	111.26	2.21	0.11	0.14	1.44
SB2	4220.20	541.73	418.00	132.16	53.32	0.46	0.18	1.93
SB3	2730.83	448.37	347.11	280.70	0.29	0.36	0.26	1.39
SB4	205.65	648.47	665.09	77.91	5.81	0.54	0.19	0.36
SB5	434.51	420.99	1045.15	634.77	1.74	0.30	0.19	0.48
SB6	439.10	411.72	709.68	394.14	1.80	0.49	0.10	0.45
SB7	251.34	404.59	808.64	283.25	4.87	0.56	0.16	0.44
SB8	216.96	357.35	567.84	360.37	0.34	0.88	0.21	0.41
SB9	169.22	340.99	464.20	90.02	1.43	0.97	0.20	0.40
SB10	217.78	367.65	540.17	126.22	4.51	1.01	0.27	0.36
SB11	204.73	465.70	530.04	110.71	1.70	1.11	0.21	0.44
SE1	226.69	415.82	640.16	1108.41	0.06	1.79	0.07	0.26
SE2	232.59	477.89	486.86	1157.95	0.09	2.44	0.21	0.15
SE3	403.70	523.42	660.69	419.55	0.07	0.23	0.31	0.09
SE4	262.50	410.34	448.00	1096.72	0.22	2.25	0.23	0.07
SE5	391.28	414.17	788.57	90.57	0.13	0.01	0.22	0.12
SE6	377.17	420.33	1083.44	111.94	0.14	0.06	0.21	0.09
SE7	331.44	480.81	212.08	234.75	0.07	0.02	0.14	0.21
SE8	354.50	499.44	159.49	173.20	0.12	0.52	0.36	0.11
SE9	408.48	407.37	698.41	1314.75	0.03	2.09	0.60	0.09
SE10	390.97	419.65	582.62	1127.39	0.09	1.92	0.23	0.24
SE11	321.35	410.60	638.49	871.45	1.49	2.44	0.28	0.28
SE12	403.25	446.55	468.57	1343.39	0.25	2.69	0.40	0.18
SE13	1233.91	557.14	906.35	1452.85	0.05	1.99	0.44	0.23
SE14	126.35	406.07	97.20	35.25	2.13	0.76	0.01	0.22
SE15	245.99	381.97	849.19	107.83	2.34	1.07	0.12	0.43
SE16	357.90	387.93	383.76	863.41	1.96	2.41	0.42	0.22
SF1	36.90	433.36	263.16	31.63	0.29	0.41	0.39	0.36
SF2	854.90	390.95	1806.97	3596.18	46.49	4.35	0.66	0.41
SAMPLE	K ($\mu\text{g g}^{-1}$)	Na (mg g^{-1})	Ca ($\mu\text{g g}^{-1}$)	Mg ($\mu\text{g g}^{-1}$)	Fe ($\mu\text{g g}^{-1}$)	Mn ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)	Cu ($\mu\text{g g}^{-1}$)
SF3	155.11	466.82	125.64	139.76	0.08	1.25	0.53	0.45
SF4	751.40	417.25	816.74	2161.76	0.02	1.08	0.53	0.56
SF5	96.76	419.06	276.91	29.58	0.05	0.38	0.47	0.49

SF6	66.38	601.08	380.69	47.10	0.09	0.37	0.50	0.44
SF7	97.38	399.55	216.54	39.35	0.64	0.34	0.46	0.53
SF8	96.32	412.15	241.43	29.59	1.09	0.01	0.59	0.39
SF9	1027.32	384.20	817.56	4094.32	61.22	3.06	0.85	0.52
SF10	789.19	391.98	1122.14	3168.05	43.38	3.43	0.77	0.48
SF11	342432.85	134.00	113.14	1066.53	0.02	0.13	0.21	0.12
SF12	2194.39	358.04	329.77	7283.19	2.71	3.12	0.63	0.43
SF13	1061.40	369.77	1593.55	3521.97	104.69	6.55	1.20	0.78
SF14	1139.28	400.52	1588.85	4431.16	47.97	3.90	0.78	0.46
SF15	103.90	375.35	145.85	21.83	0.14	0.07	0.62	0.37
SF16	1567.40	406.16	1227.42	5554.34	2.47	1.82	0.43	0.31
SP1	344.29	256.43	23.14	518.63	1.70	3.29	0.08	0.55
SP2	151.78	177.08	223.62	275.07	3.36	3.08	0.13	0.49
SP3	280.37	376.43	132.60	700.41	3.74	4.69	0.11	0.71
SP4	453.04	574.07	35.96	805.40	2.66	3.07	0.36	0.27
SP5	206.45	344.02	132.35	546.40	3.78	4.73	0.38	0.75
SP6	311.84	433.50	86.89	949.03	4.55	4.33	0.34	0.67
SP7	66.04	316.52	3.95	4.17	4.11	1.52	0.46	0.68
SP8	65.02	543.47	0.62	5.75	3.80	2.56	0.33	0.99
SP9	4030.98	379.39	1232.90	2976.78	5.63	7.08	0.59	1.03
SP10	1000.29	606.08	88.42	1848.54	6.17	2.63	0.55	1.54
SP11	1612.41	441.39	272.16	2280.77	7.95	4.86	0.85	1.40
SP12	159.13	461.24	1.03	5.65	7.16	3.21	0.71	1.38
SP13	367.05	455.70	38.14	613.47	6.03	5.20	0.56	1.08
SP14	253.32	477.42	112.80	499.11	6.21	2.70	0.55	0.89
SP15	200.77	231.65	4.36	401.22	7.12	6.79	0.84	1.32
SP16	1876.93	397.05	68.47	6063.21	8.79	5.52	0.70	1.40

Table S3. Comparison between the mean humidity and content of metals between samples with positive scores in PC2 and negative scores in PC2.

	SPAIN*		FRANCE**		PORTUGAL***	
	Group 1	Group 2	Group 1	Group 2	Group 1	Group 2
Humidity	0.3028%	0.2029%	2.1047%	0.3895%	4.3040%	0.8673%
K ($\mu\text{g g}^{-1}$)	318.63	426.40	990.22	43068.64	1700.70	381.41
Na (mg g^{-1})	446.60	437.03	386.01	409.02	472.02	381.94
Ca ($\mu\text{g g}^{-1}$)	550.09	583.69	1027.68	355.62	398.63	71.91
Mg ($\mu\text{g g}^{-1}$)	167.58	1148.48	3534.81	867.23	1777.93	948.49
Fe ($\mu\text{g g}^{-1}$)	0.72	0.47	38.33	0.59	6.73	4.65
Mn ($\mu\text{g g}^{-1}$)	0.38	2.22	3.19	0.59	4.45	3.96
Zn ($\mu\text{g g}^{-1}$)	0.20	0.32	0.76	0.45	0.67	0.40
Cu ($\mu\text{g g}^{-1}$)	0.18	0.19	0.50	0.39	1.34	0.82

* Group 1: SE3, SE5, SE6, SE7, SE8, SE14, SE15; Group2: SE1, SE2, SE4, SE9, SE10, SE11, SE12, SE13, SE16.

** Group 1: SF2, SF4, SF9, SF10, SF12, SF13, SF14, SF16; Group 2: SF1, SF3, SF5, SF6, SF7, SF8, SF11, SF15.

*** Group 1: SP9, SP10, SP11, SP16; Group 2: SP1, SP2, SP3, SP4, SP5, SP6, SP7, SP8, SP12, SP13, SP14, SP15.

Table S4. Calibration curves for quantification of mineral composition.

ELEMENT	COEFFICIENTS*			R ²
	a	b	c	
K	-4596.4	15053	40.677	0.9998
Na	-5252.0	13016	10.174	0.9999
Ca	0	0.0867	0.0036	0.9996
Mg	0	0.3877	0.0022	0.9998
Fe	-0.0050	0.1119	0.0023	0.9999
Mn	-0.0054	0.1271	0.0014	0.9999
Zn	-0.0463	0.4713	0.0021	0.9999
Cu	-0.0097	0.1908	0.0001	0.9999

* $y = ax^2 + bx + c$ with y = absorbance (a.u.) and x = concentration (ppm).

Table S5. Comparison between all DD-SIMCA models.

Data	Sample	Target	Pre-treatment	PCs	Sensitivity	Specificity
Mineral content	Prepared for FAAS	SB	Autoscaling	2	100%	95.8%
Mineral content	Prepared for FAAS	SE	Autoscaling	3	93.8%	95.3%
Mineral content	Prepared for FAAS	SF	Autoscaling	4	100%	95.3%
Mineral content	Prepared for FAAS	SP	Autoscaling	4	100%	97.8%
NIR	Dried-milled salt	SB	Mean-centering	4	100%	100%
NIR	Dried-milled salt	SE	Mean-centering	4	100%	93.0%
NIR	Dried-milled salt	SF	Mean-centering	4	100%	100%
NIR	Dried-milled salt	SP	Mean-centering	3	100%	100%
NIR	Raw salt	SB	Mean-centering	4	100%	100%
NIR	Raw salt	SE	Mean-centering	4	100%	95.3%
NIR	Raw salt	SF	Mean-centering	4	100%	83.7%
NIR	Raw salt	SP	Mean-centering	4	100%	76.7%
NIR	Dried salt	SB	Mean-centering	3	100%	95.8%
NIR	Dried salt	SE	Mean-centering	4	100%	95.3%
NIR	Dried salt	SF	Mean-centering	4	87.5%	83.7%
NIR	Dried salt	SP	Mean-centering	3	100%	72.1%

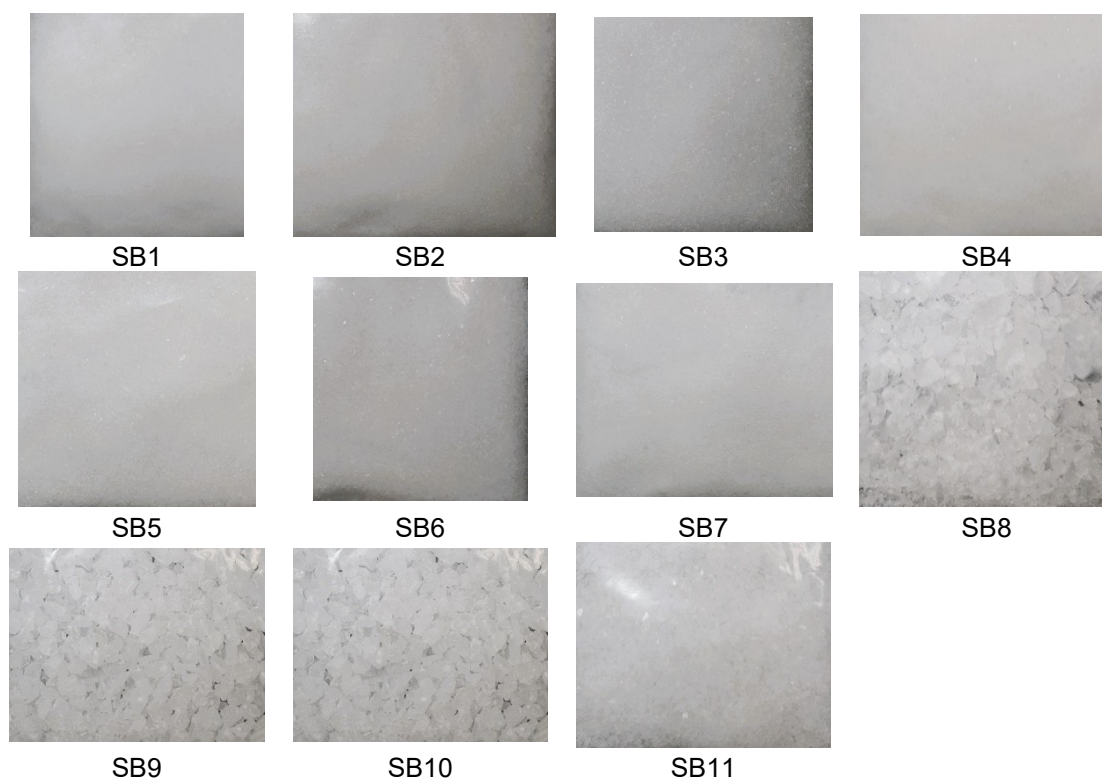


Figure S1. Raw salt from Brazil.

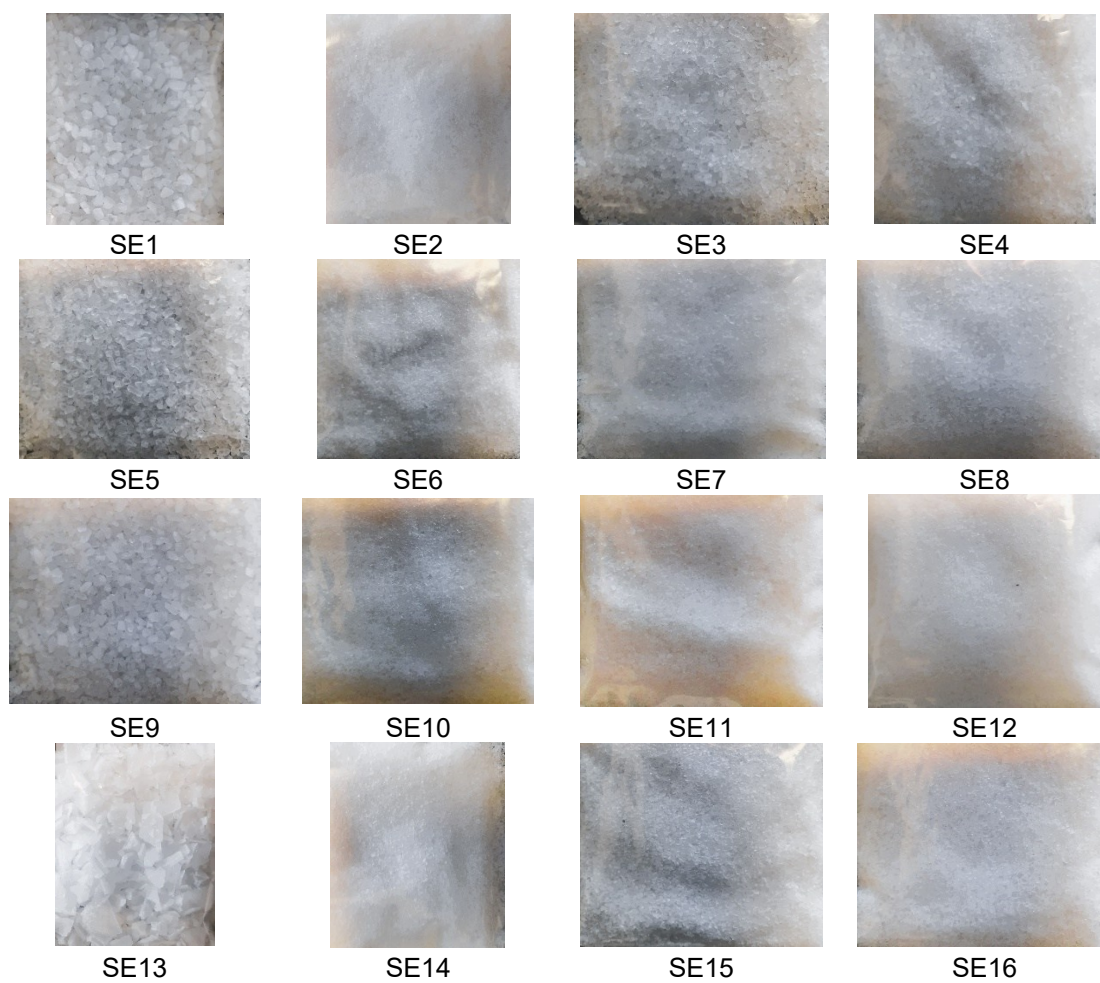


Figure S2. Raw salt from Spain.

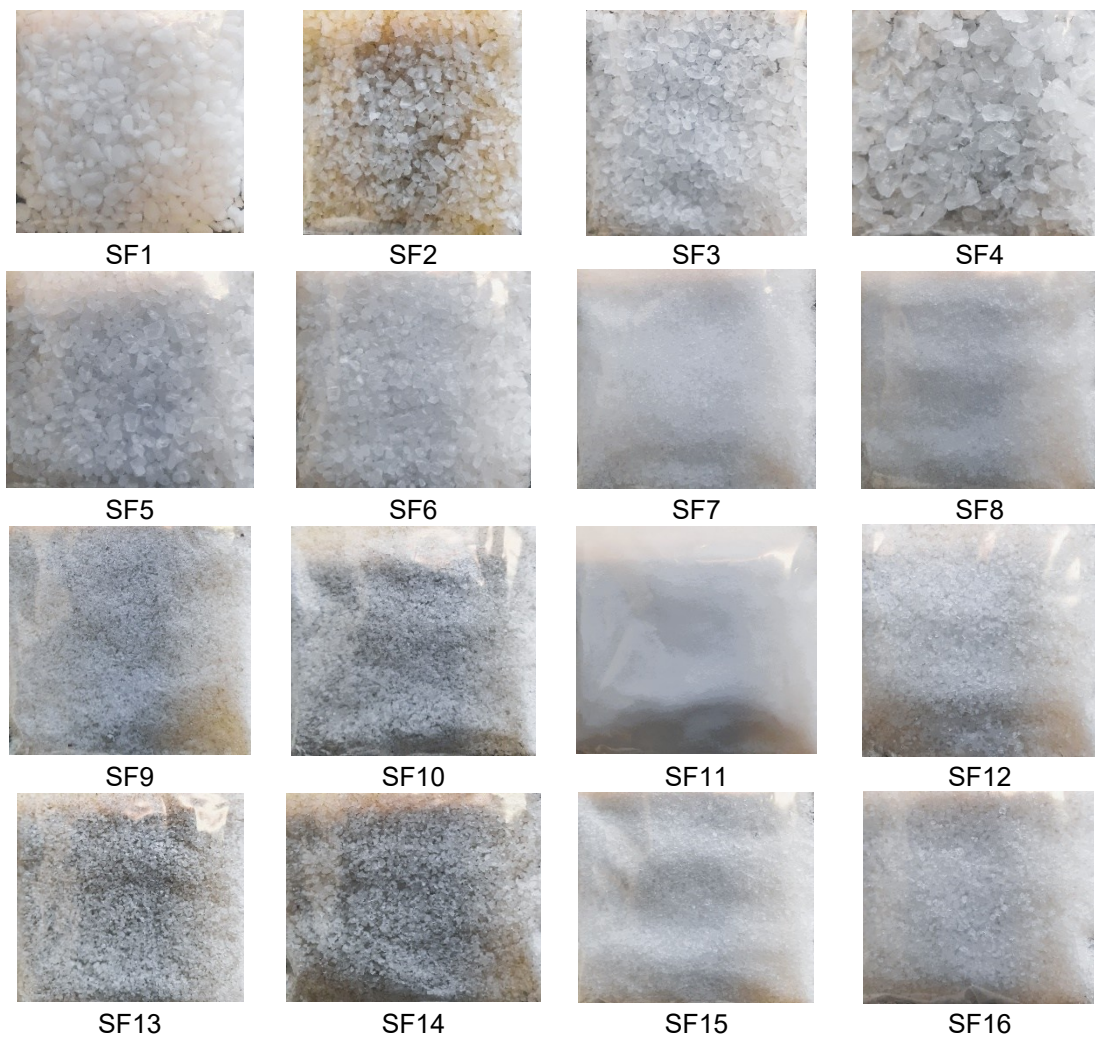


Figure S3. Raw salt from France.

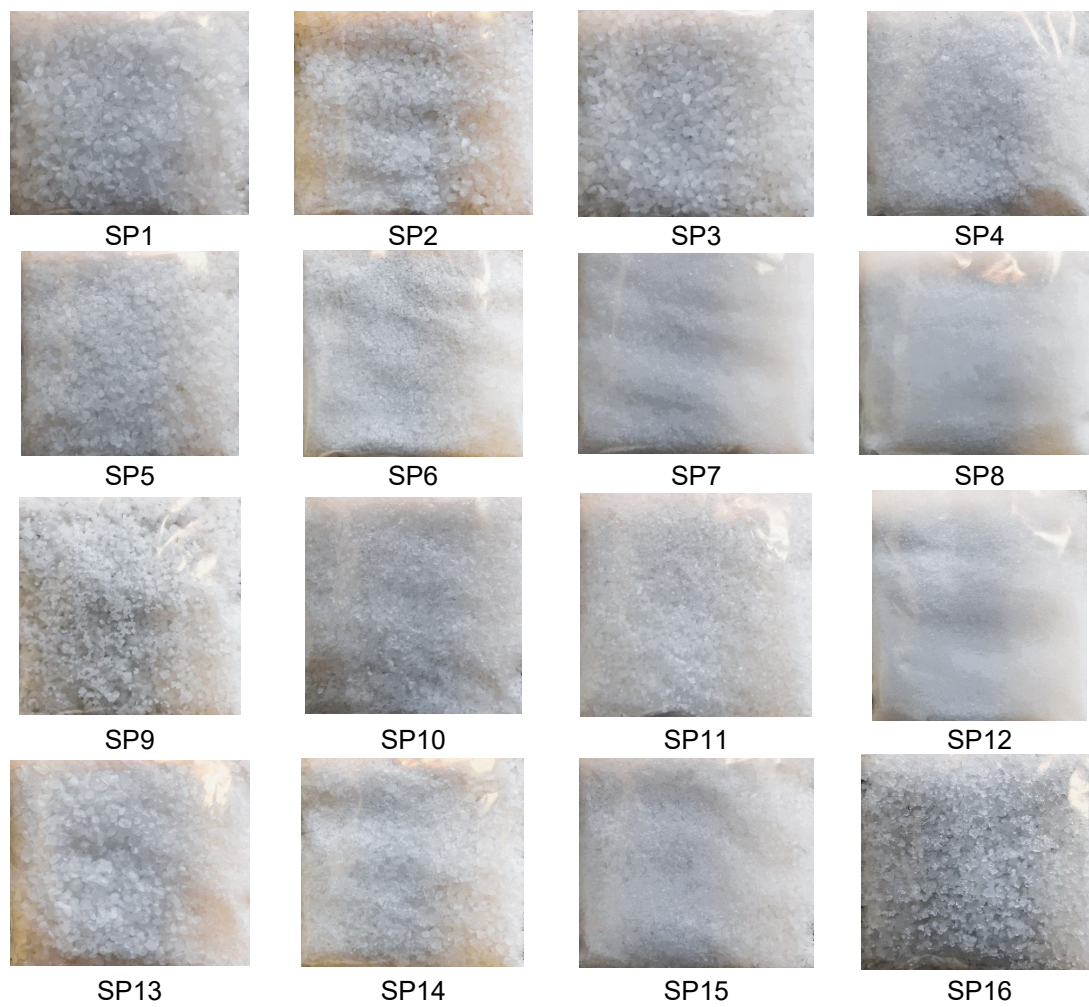


Figure S4. Raw salt from Portugal.

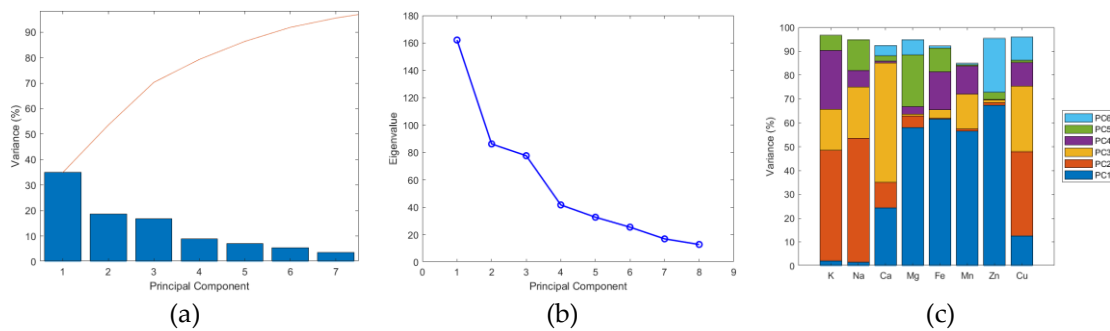


Figure S5. PCA of the autoscaled matrix of the mineral content: (a) Pareto plot with the variance and accumulated variance; (b) Scree plot with eigenvalues; (c) Bar plot with variance extracted for each variable in each principal component.

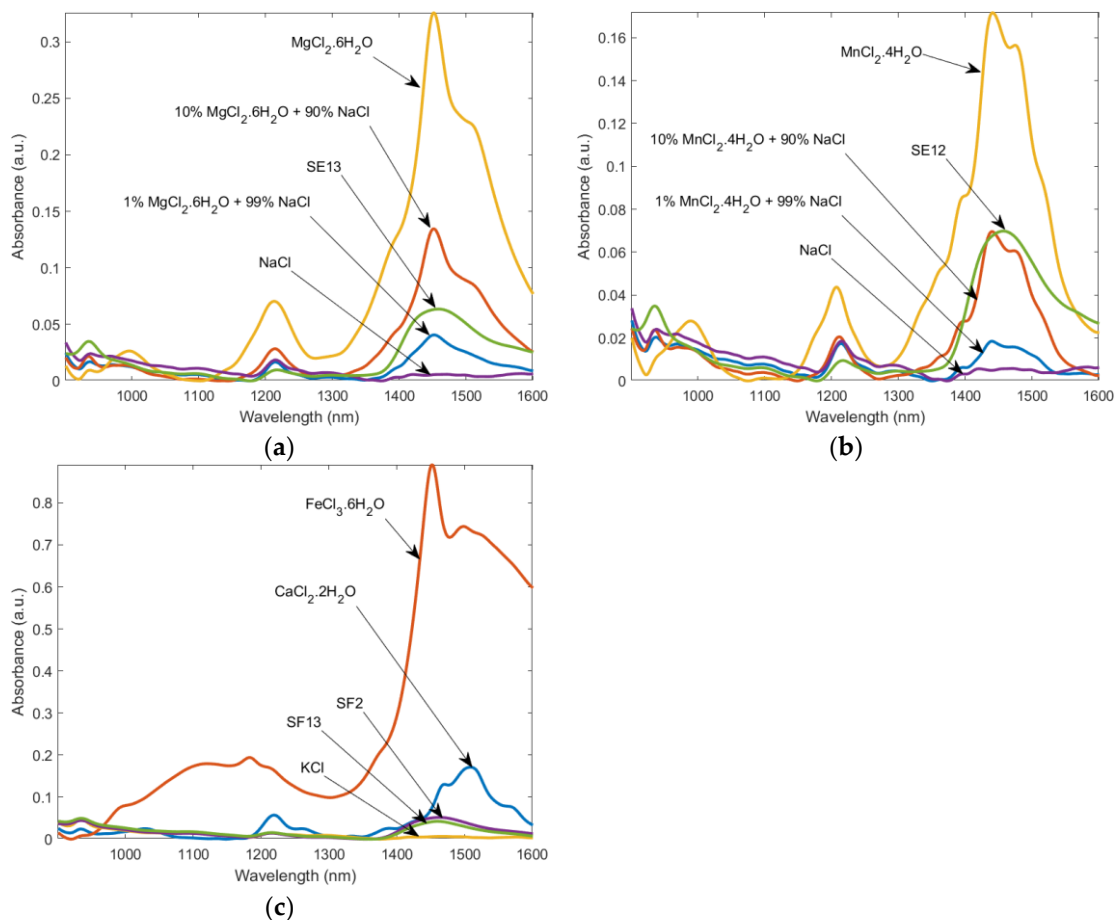


Figure S6. Comparison between NIR spectra of some salt samples, magnesium chloride hexahydrate, manganese chloride tetrahydrate, iron (III) chloride hexahydrate, calcium chloride dihydrate, sodium chloride, potassium chloride, and mixtures.

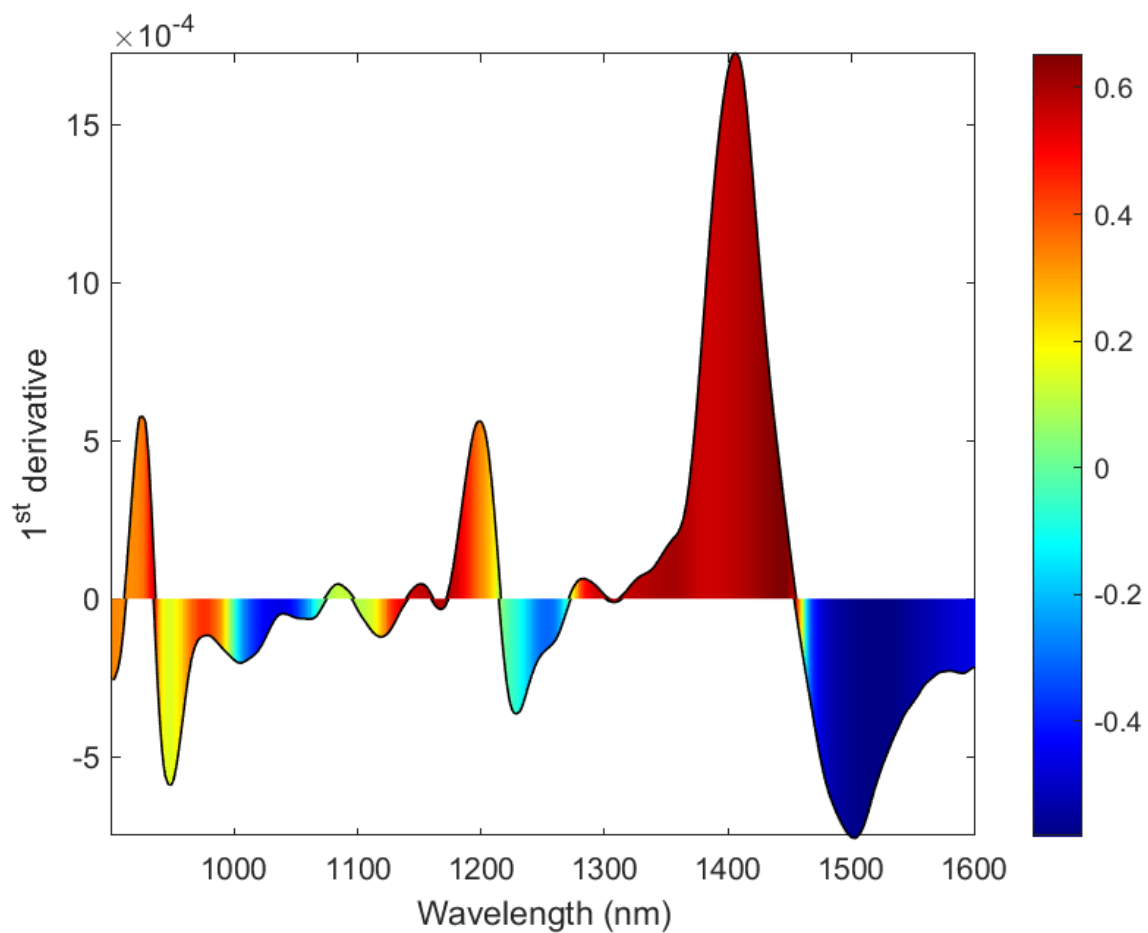


Figure S7. The correlation between the raw salt spectra' first derivative and humidity is represented by colors in the mean first derivative plot.

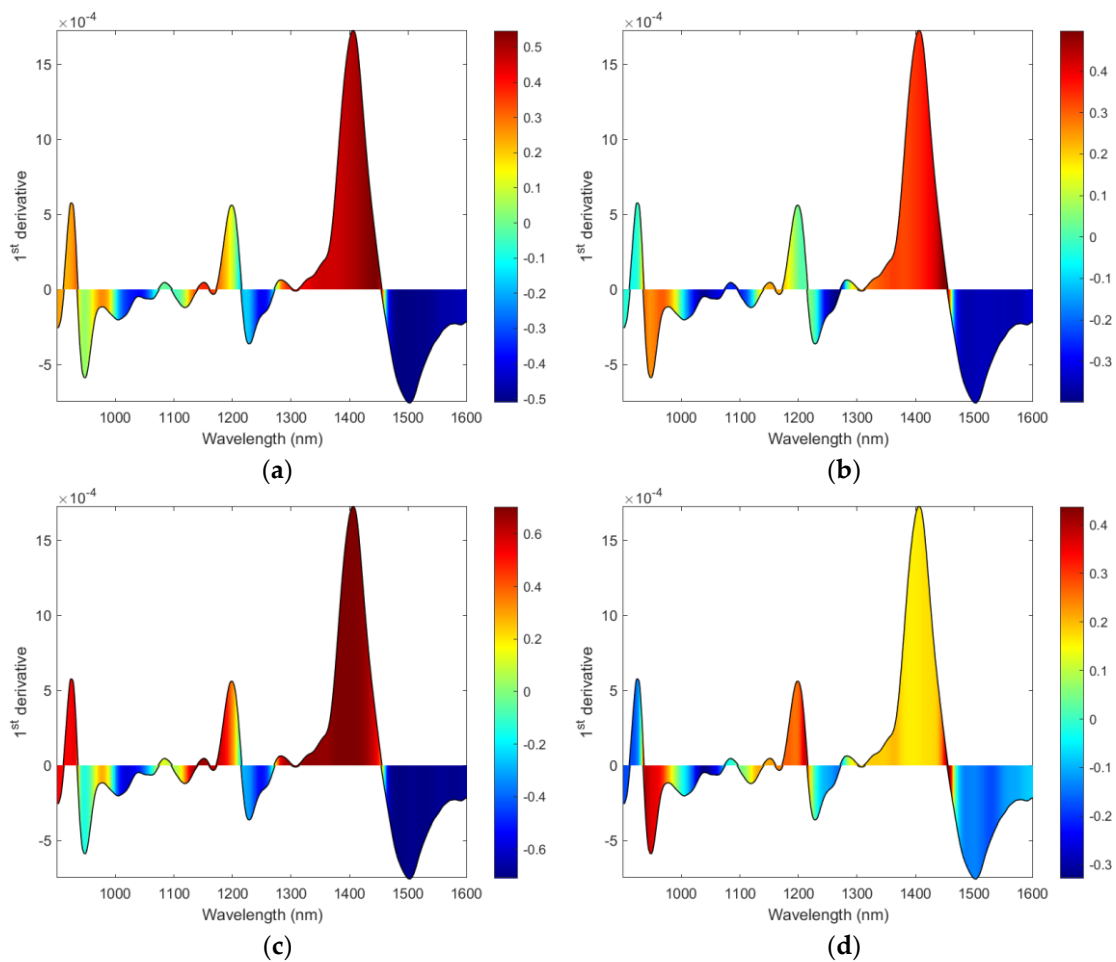


Figure S8. Correlation between the raw salt spectra' first derivative and metal content represented with colors in the mean first derivative plot: (a) Mg, (b) Fe, (c) Mn, and (d) Cu.

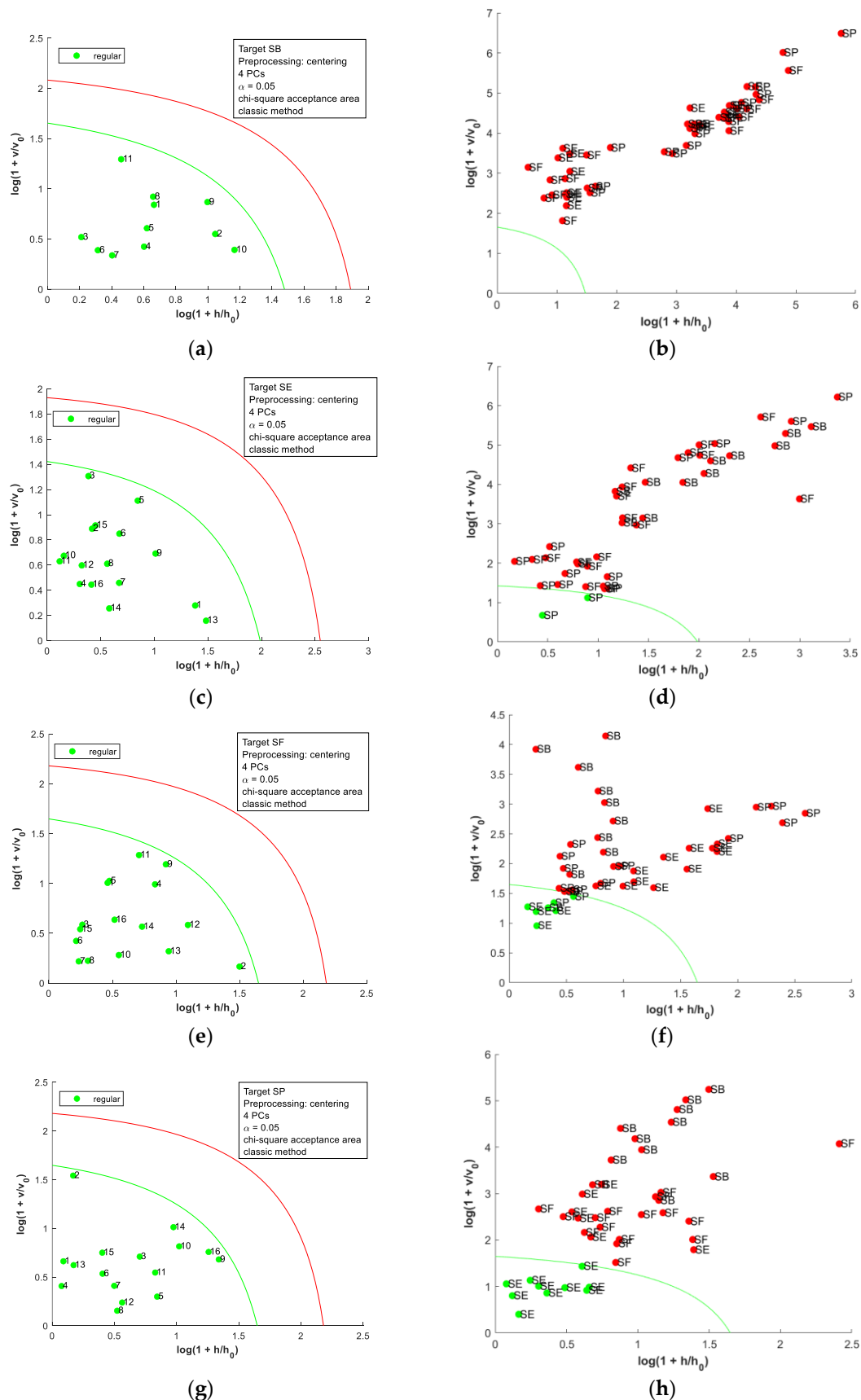


Figure S9. Acceptance plots for DD-SIMCA using the first derivative of NIR spectra from raw salt: (a) target class SB; (b) test class SE, SF, and SP; (c) target class SE; (d) test class SB, SF, and SP; (e) target class SF; (f) test class SB, SE, and SP; (g) target class SP; (h) test class SB, SE, and SF.

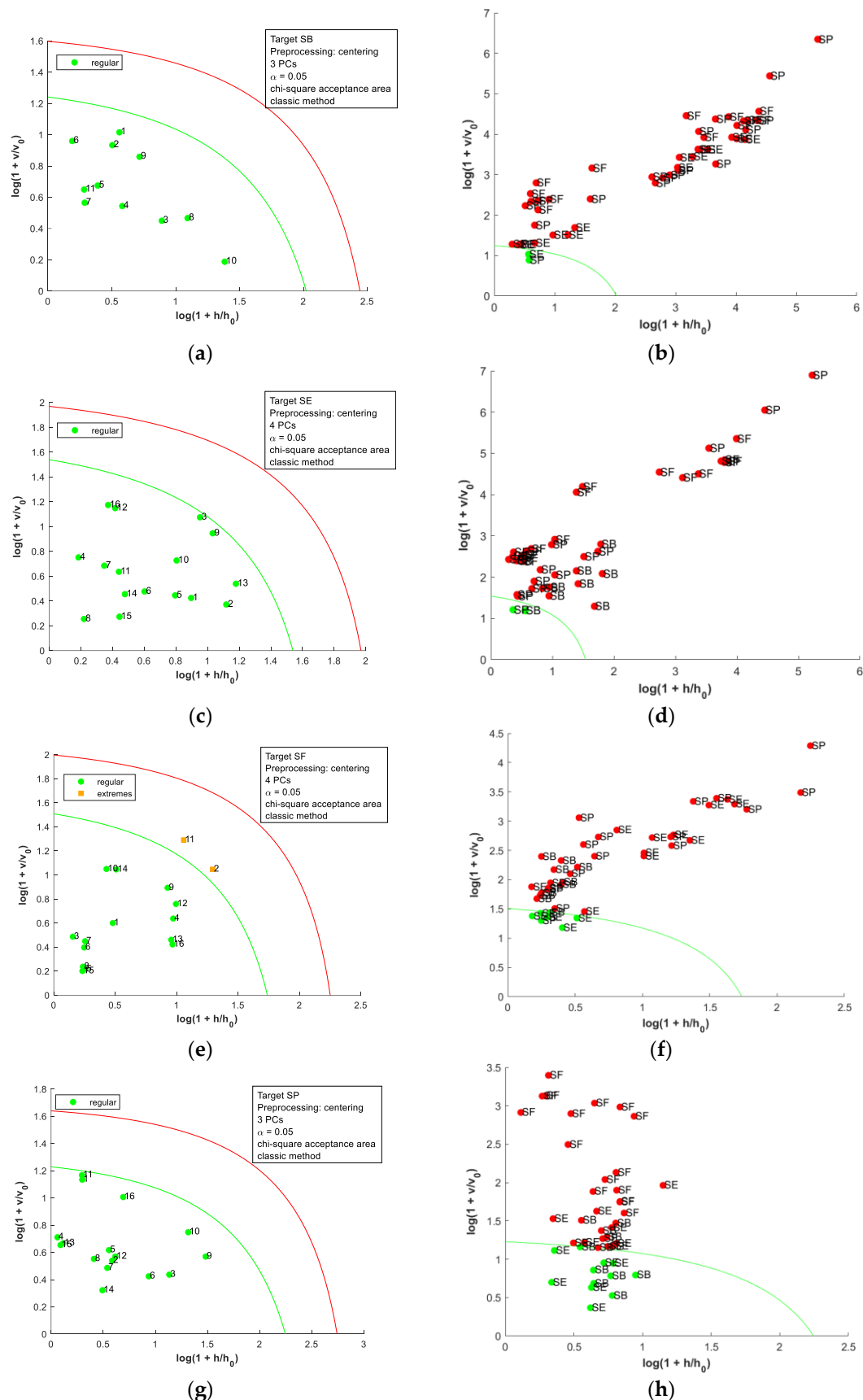


Figure S10. Acceptance plots for DD-SIMCA using the first derivative of NIR spectra from dried salt: **(a)** target class SB; **(b)** test class SE, SF, and SP; **(c)** target class SE; **(d)** test class SB, SF, and SP; **(e)** target class SF; **(f)** test class SB, SE, and SP; **(g)** target class SP; **(h)** test class SB, SE, and SF.

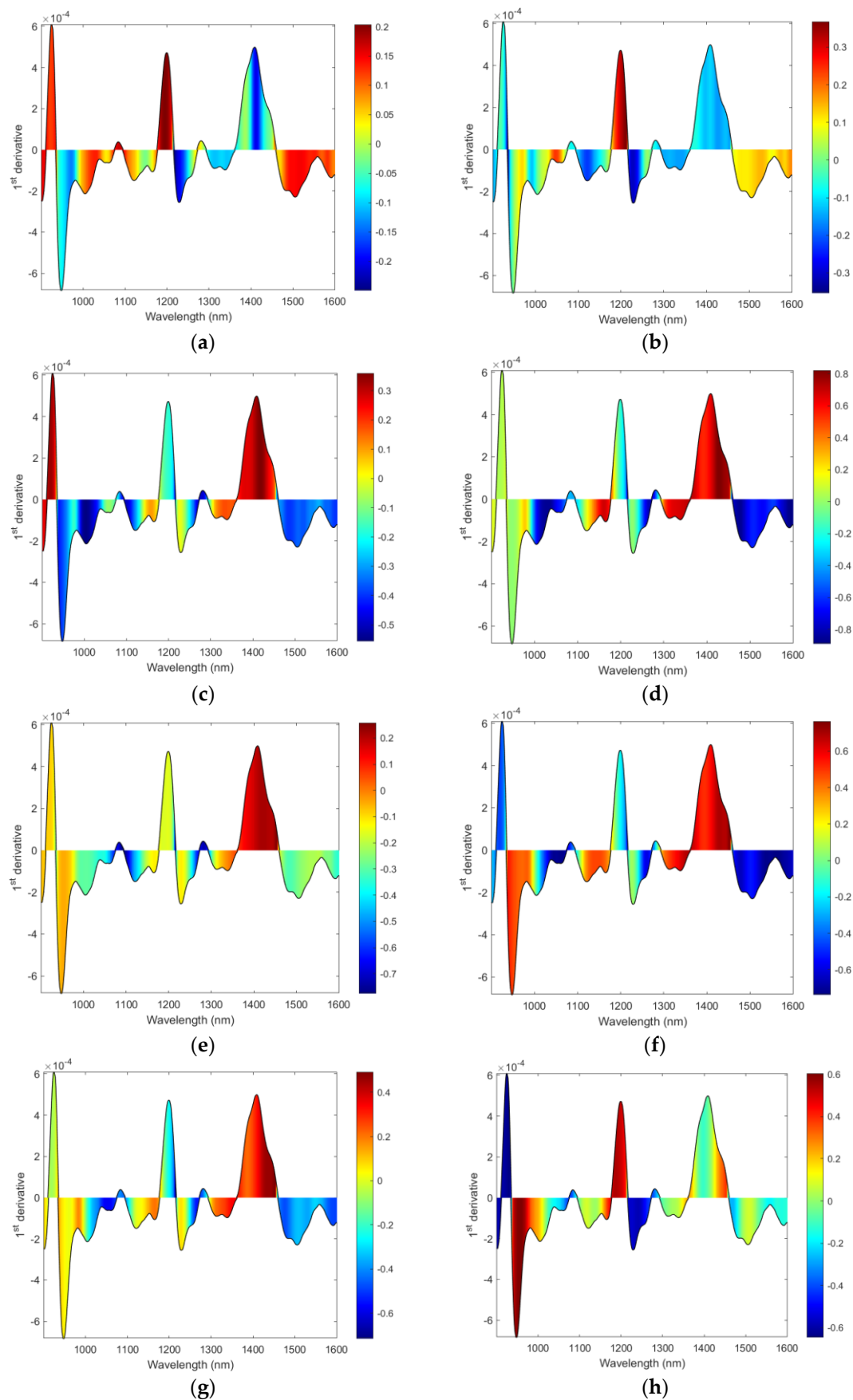


Figure S11. Correlation between the dried-milled salt spectra' first derivative and metal content represented with colors in the mean first derivative plot: (a) K, (b) Na, (c) Ca, (d) Mg, (e) Fe, (f) Mn, (g) Zn, and (h) Cu.