Quantitative imaging of element composition and mass fraction using dual-energy CT: Three-material decomposition

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In principle, dual-energy CT can only accurately decompose a mixture into two materials. To decompose a mixture into three constituent materials using dual-energy CT measurements, a third criteria must be provided to solve for three unknowns with only two spectral measurements. One solution is to assume that the sum of the volumes of three constituent materials is equivalent to the volume of the mixture (i.e., volume conservation), but this is not always true. A more generalized solution is to use the principle of mass conservation, which assumes that the sum of the masses of the three constituent materials is equivalent to the mass of the mixture. In this article, a mass-conservation based, three-material decomposition dual-energy CT algorithm is described and experimental validation of the accuracy of the technique presented. The results demonstrate that the proposed method can accurately measure elemental concentrations under low noise imaging conditions. Clinically, this may be applied to measure the mass fraction of any chemical element in a three-material mixture of solutions without the requirement of volume conservation. © 2009 American Association of Physicists in Medicine. [DOI: [10.1118/1.3097632](https://doi.org/10.1118/1.3097632)]

Key words: computed tomography (CT), dual-energy CT, dual-source CT, material decomposition

I. INTRODUCTION

A large amount of work was done on algorithms and clinical applications of material decomposition imaging using dual-energy computed tomography (CT) in the late 1970s and 1980s.^{1–9} However, despite its success in some applications, such as bone mineral density quantification, the potential of the technique in other clinical applications was not fully achieved due to limitations in generator powers, tube heat capacity, tube cooling, and spatial and temporal resolution of earlier CT systems. Recently, dual-energy CT has regained focus in terms of both basic technology and new clinical applications. The fundamental principle of dual-energy imaging is the fact that different materials have different mass attenuation coefficients when interacting with x rays. Thus, in CT images, different materials may be represented with either different or the same CT numbers depending on the materials' densities. Tabulated mass attenuation coefficients for different elements ($Z=1-92$) are available from the National Institute of Standards and Technology (NIST).^{10,11} The NIST database also has 48 compounds and mixtures, which include nearly all of the chemical elements and compounds or mixtures found in the human body. For a compound or mixture with more than one constituent element, the mass attenuation coefficient is simply the summation of weighted mass attenuation coefficients of each constituent element. The weighting factor is the mass fraction of each constituent element.^{10–12} One of the tasks of dual-energy CT imaging is to determine the mass fraction (or concentration) of a chemical element in a mixture or compound of interest from the CT images.

The mechanisms responsible for material attenuation are primarily the photoelectric effect and Compton scattering for

x-ray energies (E) in a medical diagnostic range ($E < 140$ keV). Therefore, any material's mass attenuation coefficient, excluding K edges, can be expressed as a linear combination of the coefficients of two so-called basis materials.^{8,9} The two basis materials serve as the basis vectors spanning a two dimensional space. Constituent elements different from basis materials can be viewed as a mixture of those basis materials with different mass fractions. In CT measurement, the line integral over the linear attenuation coefficient (i.e., the product of effective density and mass attenuation coefficient) can be expressed as

$$\int \mu(\mathbf{r}, E) ds = \int \rho_{\text{eff}} m_1 \mu_{m1}(\mathbf{r}, E) ds + \int \rho_{\text{eff}} m_2 \mu_{m2}(\mathbf{r}, E) ds, \quad (1)$$

where $\mu(\mathbf{r}, E)$ is the local linear attenuation coefficient, ρ_{eff} is the effective density, m_1 and m_2 are the mass fractions of basis materials 1 and 2, and $\mu_{m1}(\mathbf{r}, E)$ and $\mu_{m2}(\mathbf{r}, E)$ are the mass attenuation coefficients of basis materials 1 and 2, respectively.

Alternatively, the expected amount of photoelectric effect and Compton scattering can be approximately modeled using a material's effective atomic number, effective density, and x-ray energy (E). Instead of determining the mass fraction of each element in the material, the effective atomic number and effective density of the composite material are determined using a model of the two fundamental x-ray interactions involved. In order to differentiate this from the basis material method, we call this type of method the ρZ method in this paper. Similarly, in CT measurements, the line integral over the linear attenuation coefficient can be expressed as^{2,13}

TABLE I. Summary of previously studied dual-energy CT material decomposition algorithms.

Space	Method	
	Spectral basis (density ρ and atomic number Z)	Material basis (two materials)
Prereconstruction	Alvarez and Mackovski (Ref. 2)	Lehmann <i>et al.</i> (Ref. 8) Kalender <i>et al.</i> (Ref. 9)
Postreconstruction	Heismann <i>et al.</i> (Ref. 13)	...

$$\int \mu(\mathbf{r}, E) ds = \alpha \int \rho_{\text{eff}} \frac{Z_{\text{eff}}^k}{E^n} ds + \beta \int \rho_{\text{eff}} f_{\text{KN}}(E) ds, \quad (2)$$

where Z_{eff} is the effective atomic number, $f_{\text{KN}}(E)$ is the Klein-Nishina function, $k \approx 3-4$ and $n \approx 3-3.5$, and α and β are constants.

Both the basis material and ρZ methods described above can be implemented either in prereconstruction (projection) space or postreconstruction (image) space. The advantage of the prereconstruction implementation is that one can preprocess the raw data, for example, to correct for beam hardening. The advantage of a postreconstruction implementation lies in its relatively easy implementation and fast execution time. Examples of prereconstruction implementations include Alvarez and Mackovski's ρZ method² and Lehmann and Kalender's basis material method.^{8,9} In 2003, Heismann *et al.* implemented their ρZ method in postreconstruction space.^{12,13} Fundamentally, the ρZ method is equivalent to the basis material method, as demonstrated by Lehmann *et al.*⁸ However, the basis material decomposition method is more practical in clinical situations because it can determine the mass fraction of two materials in a mixture or compound of interest directly, as well as the effective density and effective atomic number, while the ρZ method only gives the effective density and effective atomic number of the whole mixture. Table I summarizes the currently known dual-energy methods and their properties. However, a material basis method in postreconstruction space has not been previously reported. One of the purposes of this paper is to describe the implementation of a material basis method in postreconstruction space, with experimental validation using a dual-source CT system (Somatom Definition DS, Siemens Healthcare, Forchheim, Germany).¹⁴⁻¹⁶ In non-dual-source CT systems, dual-energy measurements were previously performed by kV switching. Although modern electronics make kV switching very fast, registration problems may exist for some clinical situations.^{8,9,17} The strength of a dual-source approach to dual-energy CT is that registration problems are eliminated for postreconstruction methods.

The primary purpose of this paper, however, is to develop and test a general three-material mass-fraction decomposition using reconstructed images. The ability to decompose a mixture into its three constituent materials in the absence of volume conservation (e.g., three materials in a solution) is clinically important, such as for the purpose of quantifying

the concentration of iron in a fatty liver, when the subvoxel iron deposits can essentially be considered "in solution".

II. METHODS

II.A. Postreconstruction three-material decomposition

In principle, dual-energy CT can quantify the mass fraction of no more than two constituent materials (with known chemical compositions) in a mixture because it only provides two independent measurements. For three-material decomposition using only two different spectral measurements, one additional condition must be provided to solve for three unknowns. One solution is to assume that the sum of the volumes of three constituent materials is equivalent to the volume of the mixture (i.e., volume conservation). Explicitly, the volume fractions of three materials can be expressed as

$$f_1 + f_2 + f_3 = 1, \quad (3)$$

where f_1 , f_2 , and f_3 are the volume fractions of materials 1, 2, and 3. Therefore, the effective density ρ_{eff} of the three-material mixture is

$$\rho_{\text{eff}} = f_1 \rho_1 + f_2 \rho_2 + (1 - f_1 - f_2) \rho_3, \quad (4)$$

where ρ_1 , ρ_2 , and ρ_3 are the original densities for each material. The mass attenuation μ_m of the mixture can then be expressed as

$$\begin{aligned} \mu_m &= m_1 \mu_{m1} + m_2 \mu_{m2} + m_3 \mu_{m3} \\ &= (\rho_1 f_1 \mu_{m1} + \rho_2 f_2 \mu_{m2} + \rho_3 f_3 \mu_{m3}) / \rho_{\text{eff}}, \end{aligned} \quad (5)$$

where m_1 , m_2 , and m_3 are the mass fractions for each material. This yields four unknowns: f_1 , f_2 , f_3 , and ρ_{eff} . Equations (3) and (4) provide two additional criteria to those provided by the dual-energy measurement [Eqs. (1) and (2)]. This allows three-material decomposition using a dual-energy CT technique.

However, the constant volume assumption is not always true. For example, the volume of a salt-water mixture is not equal to the sum of the individual volumes of salt and water. Therefore, a more generalized method is needed to perform the three-material decomposition in the absence of volume conservation using dual-energy CT. We have developed a generalized three-material, mass-fraction decomposition method, where the third source of information (in addition to the dual-energy measurements) is the mixture's density, which we also obtain from the dual-energy CT images. Before we introduce our three-material decomposition method, we define the targeted three-material decomposition problem as follows.

The object under study is a mixture of three materials with known properties, such as iron, fat, and tissue. The mass fraction of each material in the mixture and the effective atomic number and effective density of the mixture are not known.

We propose a generalized three-material decomposition method based on the principle of mass conservation, where

$$m_1 + m_2 + m_3 = 1 \quad (6)$$

and m_1 , m_2 , and m_3 are the mass fractions for each material. The mixture's effective density ρ_{eff} is required; however, it is not easy to obtain because the mixture's volume is now an unconstrained variable. Our method obtains the effective density of the mixture and the constituent mass fractions from the same dual-energy CT images in two steps.

First, both the effective atomic number and effective density are obtained using a semiempirical table lookup method that can be described as a postreconstruction ρZ method approach.

Second, the effective density calculated in step 1 is used as known information and the unknowns are reduced to two mass fractions, which are solved by a semianalytical dual-energy algorithm that can be described as a material basis, postreconstruction material decomposition approach (i.e., the previously not studied category in Table I).

II.A.1. Step 1: Effective density and effective atomic number calculation

As shown in Eq. (2), we can obtain the effective atomic number and effective density of the mixture using a model of the two x-ray interaction mechanisms (i.e., photoelectric effect and Compton scattering). If the x-ray beam is monoenergetic, the effective atomic number Z_{eff} and effective density ρ_{eff} can be solved using two different x-ray beams. However, commercial CT scanners use polychromatic x-ray sources, which results in the need to consider beam hardening effects. In addition, the precision of the effective density and effective atomic number calculation using the analytical formula is limited by the precision of the model. In order to obtain the exact effective density, which is crucial to the success of our three-material decomposition algorithm, we use the semiempirical approach first introduced by Heismann *et al.*¹³ In this approach, the effective linear attenuation is modeled using the x-ray spectra $S(E)$ and detector response function $D(E)$ (Fig. 1). The model developed by Heismann *et al.* gives accurate effective density estimation for materials with effective density and effective atomic number close to water. However, it fails when dealing with materials with relatively high effective atomic number and effective density because the effect of beam hardening was not fully considered in that model. Different from the initial work of Heismann *et al.*, we use an empirical correction to the model, resulting in

$$\mu(\rho_{\text{eff}}, Z_{\text{eff}}) = C \rho_{\text{eff}} \int w(E) \mu_m(E, Z_{\text{eff}}) dE, \quad (7)$$

where $w(E) = S(E)D(E) / \int S(E)D(E)dE$ (Fig. 2) and C is an empirically determined correction factor, which is ~ 1 for $Z_{\text{eff}} < 10$ and $\sim 1.45 - (0.05 * Z_{\text{eff}})$ for $Z_{\text{eff}} \geq 10$. For dual-energy CT measurements, the ratio of the effective linear attenuation coefficients at the low energy spectrum $\mu_{\text{eff},L}$ and high energy spectrum $\mu_{\text{eff},H}$ can be expressed by

FIG. 1. Simulated x-ray beam spectra $S(E)$ (left axis) at 140 and 80 kV tube potentials. The detector response function $D(E)$ (right axis) has been calculated for the $\text{Gd}_2\text{O}_2\text{S}$ scintillator used in the CT detector.

$$\frac{\mu_{\text{eff},L}}{\mu_{\text{eff},H}} = \frac{f_L(Z_{\text{eff}})}{f_H(Z_{\text{eff}})} = F(Z_{\text{eff}}), \quad (8)$$

where

$$f_{L,H}(Z_{\text{eff}}) = \int w_{L,H}(E) \mu_m(E, Z_{\text{eff}}) dE \quad (9)$$

and

$$\rho_{\text{eff}} = \frac{\mu_{\text{eff},L}}{C f_L(Z_{\text{eff}})} = \frac{\mu_{\text{eff},L}}{C f_L[F^{-1}(\mu_{\text{eff},L}/\mu_{\text{eff},H})]}. \quad (10)$$

A numerical lookup table was constructed based on Eqs. (8)–(10) to allow determination of the effective atomic number Z_{eff} and effective density ρ_{eff} based on the ratio of the effective linear attenuation coefficients obtained from the dual-energy CT image data using the relationship

FIG. 2. Polychromatic x-ray beam weighting factor $w(E)$ at 80 and 140 kV tube potentials. The definition of $w(E)$ is expressed in Eq. (8).

TABLE II. Comparison between nominal and calculated effective densities and HA mass fraction for cylinders with different HA densities.

HA density (mg HA/cc)	Effective density			Mass fraction of HA		
	Nominal (g/cc)	Calculated (g/cc)	Error (%)	Nominal	Calculated	Error (%)
50	1.032	1.033	0.04	0.05	0.04	20
100	1.074	1.068	0.6	0.09	0.08	11
200	1.150	1.157	0.6	0.17	0.14	18
400	1.303	1.262	3	0.31	0.29	6
800	1.560	1.529	2	0.51	0.44	14
1000	1.688	1.670	1	0.59	0.51	14

$$\mu_{\text{eff},L \text{ or } H} = \left(\frac{\text{CT}_{\#L \text{ or } H}}{1000} + 1 \right) \cdot \mu_{\text{water},L \text{ or } H}. \quad (11)$$

It should be noted that Eq. (10) relies on the existence of a single value of F^{-1} . As shown by Kelcz *et al.*⁴ and Heismann *et al.*,¹³ F is a one dimensional monotonic function of effective atomic number Z and hence F^{-1} dose exist. However, F becomes a very flat curve when the effective atomic numbers are greater than 30, which indicates that the table lookup method may fail when dealing with materials with very high effective atomic numbers. Fortunately, most chemical elements in the human body are materials with low atomic numbers ($Z < 30$).

II.A.2. Step 2: Mass-fraction calculation

As discussed above, the total mass attenuation coefficient of an object containing three constituent elements is the weighted summation of the three element's mass attenuation coefficients. Thus, we model the effective linear attenuation coefficient at two different tube potentials (80 and 140 kV) as

$$\mu_{\text{eff},L} = C\rho_{\text{eff}} \int_{E=0}^{E=80 \text{ keV}} w_L(E) [m_1 \mu_{m1}(E) + m_2 \mu_{m2}(E) + (1 - m_1 - m_2) \mu_{m3}(E)] dE, \quad (12)$$

$$\mu_{\text{eff},H} = C\rho_{\text{eff}} \int_{E=0}^{E=140 \text{ keV}} w_H(E) [m_1 \mu_{m1}(E) + m_2 \mu_{m2}(E) + (1 - m_1 - m_2) \mu_{m3}(E)] dE. \quad (13)$$

In Eqs. (12) and (13), the unknowns are the mass fractions m_1 and m_2 . The mixture density ρ_{eff} is already obtained from step 1. Hence, with the dual-energy data set, we are able to solve the two unknowns m_1 and m_2 . The mass fraction of the third material is calculated using Eq. (6).

II.B. Postreconstruction two-material decomposition

The two-material decomposition can be viewed as a special case of the three-material decomposition problem. In the two-material decomposition case, one of the mass fractions

m_1 or m_2 can be preset to zero. Then, the mixture effective density and mass fractions of the two materials can be calculated as discussed above.

II.C. Experimental validation

To validate the proposed three-material and two-material decomposition methods, we performed phantom studies using two types of phantoms containing mixtures of water, hydroxyapatite [HA: $\text{Ca}_5(\text{PO}_4)_3\text{OH}$], and aqueous iron nitrate (Sigma-Aldrich®, St. Louis, MO) solutions. The calcium and iron concentrations were varied.

II.D. Two-material phantom

A total of six HA cylinders (QRM, Möhrendorf, Germany) were used in the two-material phantom. Each HA cylinder consisted of HA and water-equivalent solid materials with known mass fractions. The nominal density and mass fractions of HA and water-equivalent materials are listed in Table II. The HA cylinders were submerged in a 10 cm diameter filled cylinder, which is the central part of an anthropomorphic thorax phantom (QRM, Möhrendorf, Germany). The phantom was scanned on a dual-source CT scanner (Somatom Definition DS, Siemens Healthcare, Forchheim, Germany) using the 80/140 kV, 468/85 effective mAs, with 14×1.2 mm collimation and 0.55 pitch. The CTDI_{vol} was 17.44 mGy. In comparison, the CTDI_{vol} of our routine chest protocol (120 kV, 180 effective mAs, 64×0.6 mm collimation, 1.2 pitch) is 14 mGy. The CTDI_{vol} of our routine abdomen/pelvis protocol (120 kV, 240 effective mAs, 64×0.6 mm collimation, 1.2 pitch) is 18 mGy. Thus, the radiation level of the evaluated dual-energy scan is comparable to that of routine body CT examinations. One of the reconstructed 5 mm images of the phantom is shown in Figs. 3(a) and 3(b).

II.E. Three-material phantom

We used a 30 cm diameter water-filled cylinder containing five 1.5 cm diameter syringes filled with homogenous mixtures of water, HA, and aqueous iron nitrate (Sigma-Aldrich®, St. Louis, MO). The mass of the hydroxyapatite, iron nitrate, and water in each syringe was measured separately using a digital mass scale, resulting in a maximum error of

FIG. 3. Sample images of hydroxyapatite [$\text{HA:Ca}_5(\text{PO}_4)_3\text{OH}$] cylinders in an anthropomorphic thorax phantom at (a) 140 kV and (b) 80 kV. The HA cylinder in the center contains 100 mg HA/cm^3 . Sample images of a water, HA, and iron nitrate solution at (c) 140 kV and (d) 80 kV. The syringe centered in the middle of the water tank was filled with 1 g HA, 2 ml iron nitrate solution, and 5 ml water.

2% between the actual and nominal material masses. The nominal density and mass fractions of iron and HA are listed in Table III. The phantom was scanned on a dual-source CT scanner using the scan parameters described above. One of the reconstructed 5 mm images of the phantom is shown in Figs. 3(c) and 3(d).

III. RESULTS

III.A. Two-material decomposition

For the two-material decomposition case, the mean CT numbers of the HA cylinders ranged from 1761 to 84 HU at 80 kV and 1133 to 48 at 140 kV as the mixture effective density decreased. The effective densities of the mixtures determined using the proposed two-material decomposition algorithm were in good agreement with nominal values, with a maximum error of less than 3% and a mean error of 1.2%. The mass fractions of HA and water determined using the proposed algorithm were in reasonable agreement with nominal values, with a maximum error of approximately 20% and a mean error of 14%. The CT images at 140 and 80 kV, a color coded effective density image, and the HA mass-fraction image are shown in Fig. 4. The results for all six HA cylinders are summarized in Table II.

III.B. Three-material decomposition

For the three-material decomposition case, the mean CT numbers of the solutions ranged from 520 to 250 HU at 80 kV and 330 to 150 HU at 140 kV as the mixture effective density decreased. The effective density of the mixtures de-

termined using the proposed dual-energy CT algorithm were in good agreement with known values, with a maximum error of less than 3% and a mean error of 1.6%. The mass fractions of Ca and Fe determined using the proposed algorithm were in reasonable agreement with nominal values, with a maximum error of approximately 26% and a mean error of 13%. The color coded mass fractions of Ca and Fe are shown in Fig. 5. The results for all five solutions are summarized in Table III.

IV. DISCUSSION

Volume-conservation based algorithms for three-material decomposition can only be used for mixtures of solid materials or a solution in which one knows how the materials are mixed (i.e., have knowledge of volume displacement of the three materials when they are mixed together). The advantage of a mass-conservation based algorithm is that mass is always conserved during any chemical reaction. Using the mass-conservation based algorithm described here, our study demonstrates the feasibility of obtaining the individual mass fractions of three materials in solution using dual-energy CT.

The accuracy of three-material mass-fraction decomposition is limited on current CT systems, especially for the elements with low mass fractions. A detailed error analysis is provided in the Appendix. As shown by the error analysis, the accuracy of mass-fraction decomposition is dependent on three factors: The accuracy of the measured CT number, the accuracy of the calculated effective density, and the difference of the dual-energy ratios. The dual-energy ratio can be approximately viewed as the ratio of the mass attenuation coefficients of a chemical element at two x-ray tube potentials. The exact definition of the dual-energy ratio can be found in the Appendix.

Many factors affect CT number accuracy, such as beam hardening, scatter, and partial volume effect. These factors should be addressed in order to have as accurate CT numbers as possible when the algorithm is to be implemented using postreconstruction data. Implementation in prereconstruction (projection) space can address beam hardening errors, although scatter and partial volume effects would remain. With the relatively robust beam hardening and scattering correction algorithms of current systems, the measured CT number and calculated effective density only introduce a small amount of error in the mass-fraction decomposition process. For example, using the standard dual-energy scan protocol, we found the errors in CT number measurements and effective density calculations in our experiment to be about 5% and 2%, respectively. However, these errors may be amplified by more than ten times if the dual-energy ratios of the two elements are close. Similar results were also reported by Kelcz *et al.*⁴ Further reduction of the errors in CT number measurements and effective density calculations are possible but difficult because the measurement uncertainties are already close to the current system limit. Therefore, the most critical factor in material mass-fraction decomposition is the dual-energy ratios of the two elements in the tissue, as discussed in the Appendix.

TABLE III. Experiment validation of three-material mass-fraction decomposition of mixtures.

Mixtures	Effective density			Mass fraction of Ca (%)			Mass fraction of Fe (%)		
	Nominal (g/cc)	Calculated (g/cc)	Error (%)	Nominal	Calculated	Error	Nominal	Calculated	Error
1 g HA ^a +2 ml iron nitrate +1 ml water	1.19	1.18	0.7	9.9	9.1	8	0.90	0.97	7
1 g HA +2 ml iron nitrate +2 ml water	1.15	1.13	1.3	7.9	8.5	7	0.72	0.67	6
1 g HA +2 ml iron nitrate +3 ml water	1.12	1.09	2.5	6.6	8.3	26	0.60	0.62	3
1 g HA +2 ml iron nitrate +4 ml water	1.10	1.08	1.8	5.7	6.4	13	0.52	0.54	5
1 g HA +2 ml iron nitrate +5 ml water	1.09	1.07	1.5	5.0	5.6	12	0.45	0.53	18

^aHA:Ca₅(PO₄)₃OH.

To reduce the noise amplification effect using current dual-energy CT systems, one effective method is to use added x-ray beam filtration. We have demonstrated that a factor of 3 improvement in the difference of dual-energy ratios can be obtained by use of a 0.5 mm tin filter in the 140 kVp beam.¹⁸ Another promising technique, which may be available clinically in the next three to five years, is the use of energy resolving photon counting detectors.^{19,20} Several other new x-ray CT techniques also have been proposed recently, including use of monoenergetic x-ray beams, phase-contrast imaging, and time-of-flight imaging.^{21,22} However, it may take a significant amount of time for these techniques to reach clinical utility.

V. CONCLUSION

We have developed a generalized three-material mass-fraction decomposition algorithm for dual-energy CT. Experimental data demonstrate the feasibility of the proposed algorithm to determine the mass fraction of three materials of known chemical element compositions using dual-energy CT measurements and without the constraint of volume conservation. The method developed here can be used in clinical

applications involving the separation of three known materials in a solution. The accuracy of this method is heavily dependent on the dual-energy ratios of the two elements in the mixture.

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APPENDIX: ERROR ANALYSIS

Here, we describe in greater detail the error propagation in our dual-energy material decomposition method. To simplify the mathematical derivation and focus on the error propagation, we assume that the dual-energy measurements are made with two monochromatic x-ray beams of high energy E_H and low energy E_L . Equations (12) and (13) are rewritten here as

FIG. 4. CT images of six hydroxyapatite (HA) cylinders at (a) 140 and 80 kV tube potentials. The color coded effective density image (b) and HA mass-fraction image (c) are also shown.

FIG. 5. Color coded mass fractions of calcium (a) and iron (b) in the mixed solutions. The chemical densities and mass fractions of calcium and iron are listed in Table III.

$$\mu_{\text{eff},L} = \rho_{\text{eff}}[m_1\mu_{m1,L} + m_2\mu_{m2,L} + (1 - m_1 - m_2)\mu_{m3,L}], \quad (\text{A1})$$

$$\mu_{\text{eff},H} = \rho_{\text{eff}}[m_1\mu_{m1,H} + m_2\mu_{m2,H} + (1 - m_1 - m_2)\mu_{m3,H}]. \quad (\text{A2})$$

The above equations can be rearranged into matrix formation,

$$\begin{bmatrix} \mu_{m1,L} - \mu_{m3,L} & \mu_{m2,L} - \mu_{m3,L} \\ \mu_{m1,H} - \mu_{m3,H} & \mu_{m2,H} - \mu_{m3,H} \end{bmatrix} \begin{bmatrix} m_1 \\ m_2 \end{bmatrix} = \begin{bmatrix} \frac{\mu_{\text{eff},L}}{\rho_{\text{eff}}} - \mu_{m3,L} \\ \frac{\mu_{\text{eff},H}}{\rho_{\text{eff}}} - \mu_{m3,H} \end{bmatrix}. \quad (\text{A3})$$

To have a unique solution for Eq. (A3), the coefficient matrix must be nonsingular (i.e., the determinant of the coefficient matrix is nonzero). The determinant of the coefficient matrix is

$$\begin{vmatrix} \mu_{m1,L} - \mu_{m3,L} & \mu_{m2,L} - \mu_{m3,L} \\ \mu_{m1,H} - \mu_{m3,H} & \mu_{m2,H} - \mu_{m3,H} \end{vmatrix} = (\mu_{m1,L} - \mu_{m3,L}) \times (\mu_{m2,H} - \mu_{m3,H}) - (\mu_{m2,L} - \mu_{m3,L})(\mu_{m1,H} - \mu_{m3,H}). \quad (\text{A4})$$

If we assume that the third material in the mixture is water (i.e., tissue equivalent material), we can define B,

$$B_{i,E} = \frac{\mu_{mi,E} - \mu_{m3,E}}{\mu_{m3,E}} \times 1000, \quad i = 1, 2, \quad E = L, H. \quad (\text{A5})$$

Then, it can be derived from Eq. (A4) that the nonsingular condition is satisfied only if the dual-energy ratios (R_1 and R_2) of the other two elements in the mixture are not equal, as shown by

$$\left(R_1 = \frac{B_{1,L}}{B_{1,H}} \right) \neq \left(R_2 = \frac{B_{2,L}}{B_{2,H}} \right). \quad (\text{A6})$$

If the dual-energy ratios of the two elements are close, the problem is ill conditioned, which leads to unstable solutions.

Using the above definitions of B and dual-energy ratio, the solution of Eq. (A3) can be expressed as follows:

$$m_1 = \frac{1000}{B_{1,H}} \cdot \frac{\left[\frac{\mu_{\text{eff},L}}{\rho_{\text{eff}}\mu_{m3,L}} - 1 + R_2 \left(1 - \frac{\mu_{\text{eff},H}}{\rho_{\text{eff}}\mu_{m3,H}} \right) \right]}{(R_1 - R_2)}, \quad (\text{A7})$$

$$m_2 = \frac{1000}{B_{2,H}} \cdot \frac{\left[\frac{\mu_{\text{eff},L}}{\rho_{\text{eff}}\mu_{m3,L}} - 1 + R_1 \left(1 - \frac{\mu_{\text{eff},H}}{\rho_{\text{eff}}\mu_{m3,H}} \right) \right]}{(R_1 - R_2)}. \quad (\text{A8})$$

If we neglect the errors caused by using water as the tissue equivalent material and assume independent errors in μ_{eff} and ρ_{eff} of $\sigma(\mu_{\text{eff}})$ and $\sigma(\rho_{\text{eff}})$, respectively, the errors in mass-fraction calculation ($\sigma^2(m)$) can be approximately expressed by

$$\sigma^2(m) \propto \frac{1}{(R_1 - R_2)^2} \left[\frac{1}{\rho_{\text{eff}}^2 \mu_{m3}^2} \sigma^2(\mu_{\text{eff}}) + \frac{\mu_{\text{eff}}^2}{\rho_{\text{eff}}^4 \mu_{m3}^2} \sigma^2(\rho_{\text{eff}}) \right]. \quad (\text{A9})$$

Here, we also neglect the small difference of mass attenuation coefficients of water at low and high energies. For a dilute solution, the effective mass attenuation coefficient of the solution is close to the mass attenuation coefficient of water (i.e., $\mu_{\text{eff}} \approx \mu_{m3}$), so Eq. (A9) can be written in a more compact form,

$$\sigma^2(m) \propto \frac{1}{(R_1 - R_2)^2} \left[\frac{\sigma^2(\mu_{\text{eff}})}{\mu_{\text{eff}}^2} + \frac{\sigma^2(\rho_{\text{eff}})}{\rho_{\text{eff}}^2} \right]. \quad (\text{A10})$$

Equation (A10) indicates that the accuracy of the mass-fraction determination is dependent on three factors: The accuracy of the measured CT numbers, the accuracy of the calculated effective density, and the difference of the dual-energy ratios. For two elements in a three-material mixture having similar attenuation coefficient energy dependencies (i.e., $R_1 \approx R_2$), the error (noise) would be amplified. The result shown here is similar to that reported by Kelcz *et al.*⁴ As an example, if we assume that the effective x-ray beam energies are 50 and 80 keV for low and high tube potentials, respectively, then the dual-energy ratios for calcium (Ca) and iron (Fe) are 4.05 and 3.75, respectively. The small difference (0.3) between dual-energy ratios will amplify the measurement uncertainty by a factor of 11.

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